# The influence of weathering and organic matter on heavy metals lability in silicatic, Alpine soils

Egli, M ; Sartori, G ; Mirabella, A ; Giaccai, D ; Favilli, F ; Scherrer, D ; Krebs, R ; Delbos, E

Abstract: We investigated the effect of organic matter and weathering on the lability and solid phase speciation of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) in two contrasting subalpine regions in the Italian Alps. Cr, Ni and Cu could be linked to weathering. This was not the case for Pb. Since organic matter (OM) influences the solid phase speciation of heavy metals, the total organic C and N content, the C and N content of different density fractions of OM and also of the labile (oxidised by H2O2) and stable (H2O2-resistant) fractions were determined. Soil OM stocks were high and soils on north-facing slopes had more OM than the south-facing sites to which they were paired. Density measurements and the H2O2 fractionation indicated that the higher OM content on north-facing sites was due to an accumulation of weakly degraded organic material. Due to higher weathering intensity on north-facing sites, the abundance of the EDTA-extractable heavy metals was higher than on south-facing sites. All EDTA-extractable heavy metals showed a good correlation to the water-soluble phenolic concentrations which indicates that the metals were probably translocated as metalorganic complexes. Pb and Cu correlate not only to the light (density b1 g/cm3) and labile, organic fraction but also to the heavy (densityN2g/cm3) and stable fraction. High-mountain ecosystems like the Alps are sensitive to changing environmental conditions such as global warming. A warmer climate and the more favourable conditions it brings for biological activity, especially at cooler sites, will probably lead in the short- to mid-term to an increased loss of accumulated, weakly degraded OM. As the Pb and Cu content is significantly related to the labile organic matter pools, the risk exists that an increase in OM mineralisation could affect the storage capacity and mobility of these metals in soils.

DOI: https://doi.org/10.1016/j.scitotenv.2009.10.005

# The influence of weathering and organic matter on heavy metals lability in silicatic, Alpine soils

Markus Egli[a,*], Giacomo Sartori[b], Aldo Mirabella[c], Daniele Giaccai[c], Filippo Favilli[a], Daniel Scherrer[d], Rolf Krebs[d], Evelyne Delbos[e]

[a]Department of Geography, University of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

[b]Museo Tridentino di Scienze Naturali, Via Calepina 14, 38100 Trento, Italy

[c]Istituto Sperimentale per lo Studio e la Difesa del Suolo, Centro di ricerca per l'agrobiologia e la Pedologia CRA-ABP, Piazza D'Azeglio 30, 50121 Firenze, Italy

[d]Institute of Natural Resource Sciences, Zurich University of Applied Sciences, Grüental, 8820 Wädenswil, Switzerland

[e]Macaulay Institute, Craigiebuckler, Aberdeen AB15 8QH, UK

*corresponding author:
tel. +41 44 635 51 14
fax: +41 44 635 68 48
e-mail: markus.egli@geo.uzh.ch

**Abstract**

We investigated the effect of organic matter and weathering on the lability and solid phase speciation of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) in two contrasting subalpine regions in the Italian Alps. Cr, Ni and Cu could be linked to weathering. This was not the case for Pb. Since organic matter (OM) influences the solid phase speciation of heavy metals, the total organic C and N content, the C and N content of different density fractions of OM and also of the labile (oxidised by $H_2O_2$) and stable ($H_2O_2$-resistant) fractions were determined. Soil OM stocks were high and soils on north-facing slopes had more OM than the south-facing sites to which they were paired. Density measurements and the $H_2O_2$ fractionation indicated that the higher OM content on north-facing sites was due to an accumulation of weakly degraded organic material. Due to higher weathering intensity on north-facing sites, the abundance of the EDTA-extractable heavy metals was higher than on south-facing sites. All EDTA-extractable heavy metals showed a good correlation to the water-soluble phenolic concentrations which indicates that the metals were probably translocated as metal-organic complexes. Pb and Cu correlate not only to the light (density < 1 g/cm$^3$) and labile, organic fraction but also to the heavy (density > 2 g/cm$^3$) and stable fraction. High-mountain ecosystems like the Alps are sensitive to changing environmental conditions such as global warming. A warmer climate and the more favourable conditions it brings for biological activity, especially at cooler sites, will probably lead in the short- to mid-term to an increased loss of accumulated, weakly degraded OM. As the Pb and Cu content is significantly related to the labile organic matter pools, the risk exists that an increase in OM mineralisation could affect the storage capacity and mobility of these metals in soils.

**Keywords:** heavy metals, soil organic matter, weathering, Alpine soils, density fractions, labile OM, climate

## Introduction

The capacity of soils to retain and release elements is an essential part of their function. Soils play a major role in the biogeochemical cycle, including weathering and the storage of nutrients and carbon (Bain et al., 1994; Richter et al., 2007). Bedrock lithology, ore occurrences and urban contamination all have an influence on the element concentrations in soils and consequently in plants (e.g. Reimann et al., 2007a). Over the last few decades much attention has been paid towards soil pollution involving excess levels of both the essential micronutrients and some of the non-essential, potentially-toxic trace elements such as Cd and Pb. The major external source of heavy metals in soils is usually contamination caused by anthropogenic activities, such as metal mining, smelting and processing or the use of fossil fuels. Additionally, diffuse pollution by wet and dry deposition has resulted in the long-term accumulation of heavy metals in many parts of the world, for example in Greenland ice (Rosman et al., 1993), peat bogs (Weiss et al., 1999) and remote Alpine and subarctic soils (Bindler et al., 1999; Nowack et al., 2001). In remote Alpine areas (Swiss National Parc), Nowack et al. (2001) measured increased Pb concentrations in the topsoil which could not be explained by weathering processes. The measurement of Pb-isotopes ratios ($^{206}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{207}Pb$) indicated that the enrichment of lead is largely attributed to atmospheric input. Some high metal concentrations in soils can also be due to natural origin (D'Amico et al., 2008). High to very high concentrations of Cr and Ni were reported for soils developed on mafic to ultra-mafic parent material (Gasser et al., 1995; Salvador-Blanes et al., 2006; D'Amico et al., 2008). Pedogenetic processes may release large quantities of potentially hazardous trace metals (D'Amico et al., 2008). Weathering of bedrock with only slightly elevated metal concentrations may result in an enrichment of heavy metals, i.e. of sparingly soluble elements as residual after dissolution and leaching of the more soluble major elements, by pedogenic processes (e.g. Blaser et al., 2000).

Weathering rates of soils can be derived with the help of concentration profiles of immobile

elements such as Ti or Zr. A prerequisite for the comparison of different soils is that they have a similar age. Long-term weathering rates can be determined by comparing the chemistry and mineralogy of soil profiles of known age and the fresh source rock composition (April et al. 1986; Eggenberger 1995). Such calculations are often based on enrichment/depletion factors determined using immobile element contents (e.g. Green et al., 2006; Riebe et al. 2004a,b; Egli et al., 2008).

The mass balance and enrichment factor (EF) approach can be used to quantify accumulation or depletion of metals in a soil profile by considering the abundance of the metal of interest, relative to the abundance of a conservative, lithogenic element (Bowen, 1979; Brimhall and Dietrich, 1987). Enrichment factors (EF) are often used to quantify the extent of human-induced contamination (Blaser et al., 2000; Reimann and de Caritat, 2000). Reimann and de Caritat (2005) showed, however, that the EF may strongly be influenced by, among other factors, biogeochemical processes that redistribute chemical elements between environmental compartments at the earth's surface. Differences between the mineral soils and the organic layer are distinct. The O-horizon does no longer solely depend on the underlying soil but is strongly impacted by the uptake characteristics of the plants at the sample site. Therefore, calculations using the EF approach have to be considered with caution. Furthermore, two important assumptions concerning elemental components are required in the mass balance and also EF calculations using immobile elements (White and Blum, 1995). The first involves the determination of the composition of the parent material. Soils must have developed on a homogeneous parent material. The second requirement is that weatherable elements must be ratioed against an inert component *i*, present in both the parent material and the soil. Ti, Zr or V are often considered to be almost immobile (Chadwick et al., 1990; White and Blum, 1995). Only small variations in bedrock lithology can lead to significant errors in the calculation of mass balances (cf. Egli et al., 2003). From this point of view, the use of Ti as a tracer has a non-negligible advantage because it usually occurs in much higher concentrations

than Zr, V or any other “reference element”. Stiles et al. (2003) concluded that Ti is better suited for mass-balance calculations during pedogenesis as Ti is present in higher concentrations and is enriched in the clay fraction. Taking these limitations into account, mass balance measurements are a reasonable tool to estimate accumulation or weathering losses of elements.

One main aim of this paper is to calculate weathering losses of major and minor (heavy metals) compounds and to relate the chemical behaviour of heavy metals to soil properties in an Alpine environment.

The currently occurring worldwide climate changes are fuelling a growing interest in the effects of climate and time on the landscape, soil evolution and in particular soil organic matter. It is known that several heavy metals have a specific affinity to soil organic matter. Soil organic matter characteristics therefore influence substantially the mobility of heavy metals in soil. Climate change is assumed to alter to a certain extent soil organic matter quality and quantity (e.g. Fissore et al., 2008; Schmitt et al., 2008). Very little is known how this could affect the biogeochemical behaviour of heavy metals in Alpine soils. An additional aim was therefore to investigate the relationship of heavy metals to organic matter fractions and to derive hypotheses for possible future trends.

## Materials and methods

### *Study area*

Eight soil profiles were investigated in the subalpine range on a siliceous parent material in Val di Rabbi and Val di Fassa in northern Italy (Table 1). Four of these profiles were north-facing and the other four south-facing. To facilitate comparisons between soils on north and

127 south slopes, the altitudes of the sites were as similar as possible. All soils have an age (time
128 since deglaciation) of about 17000 years (Favilli et al., 2009).
129 The description of the soil profiles and designation of soil horizons was done according to the
130 FAO protocol (FAO, 1998; IUSS Working Group WRB, 2006). Horizon designation, based
131 on field data (like Munsell-colour, structure, horizon thickness etc.), has been verified using
132 chemical data. The soils were Cambic Umbrisols, Umbric, Entic or Albic Podzols (IUSS
133 Working Group WRB, 2006; Table 1). Soils in Val di Rabbi developed on paragneiss
134 (morainic material) and those in Val di Fassa on basaltic latite (morainic material). According
135 to the Soil Taxonomy (Soil Survey Staff, 2006), the soil moisture regime was udic (humid
136 conditions, < 90 days/year with a dry soil) at all sites and the soil temperature regime was
137 cryic (mean annual temperature < 8 °C, no permafrost). Maximum precipitation occurs during
138 the summer and autumn months.
139
140 *Soil sampling*
141 The eight profiles were selected during an inventory of the characteristics and variability of
142 the different soil types. The chosen soils were assumed to be representative of the altitudinal
143 zones and exposure. Special attention was given to ensure that the soils showed an
144 undisturbed evolution (according to their macromorphology) with no signs of erosion or
145 burial.
146 As soil horizons are considered to be identical compartments having typical chemical and
147 mineralogical processes, sampling was bound to the morphology of the soils. Around two to
148 four kilograms of soil material (Hitz et al., 2002) were collected per soil horizon from the 8
149 soil pits. Soil bulk density was determined by a soil core sampler (or by excavated holes to a
150 volume of about 500 – 2000ml that were backfilled with a measurable volume of quartz
151 sand). Undisturbed soil samples were taken down to the BC or C horizon.
152

153 *Soil chemistry and physics*

154 The soil samples were air-dried, large aggregates were gently broken by hand and sieved to <
155 2 mm. Total C and N contents of the soil were measured with a C/H/N analyser (Elementar
156 Vario EL, Elementar Analysensysteme GmbH) using oven-dried and ball-milled fine earth.
157 Total C corresponds in our case to organic C due to the absence of any carbonates in the soil.
158 Soil pH (in 0.01 M $CaCl_2$) was determined on air-dried samples of the fine earth fraction
159 using a soil solution ratio of 1:2.5.
160 Element pools (light elements and some heavy ones) in the soil (Ca, Mg, K, Na, Fe, Al, Mn,
161 Si, Ti) were determined by a total dissolution method. Fine earth (< 2 mm in diameter) and
162 soil skeleton (>2 mm up to 200 mm) were separately analysed. Oven-dried samples (fine
163 earth and crushed soil skeleton samples) were dissolved using a mixture of HF, HCl, $HNO_3$,
164 and $H_3BO_3$ in a closed system (Hossner, 1996) (microwave oven under high pressure, 25 bar).
165 Concentrations were determined by AAS (Atomic Absorption Spectrometry – AAnalyst 700,
166 Perkin Elmer, USA). The oxalate-extractable iron and aluminium fractions ($Fe_o$, $Al_o$) were
167 determined according to McKeague et al. (1971) and analysed by AAS. The total heavy metal
168 (Cd, Cr, Cu, Ni, Pb and Zn) composition of the soil skeleton and fine earth samples was
169 analysed by X-ray fluorescence spectrometry (XRF). The soil skeleton samples had to be
170 crushed to a size of <1mm. Around 6 g of soil skeleton or fine earth material were milled to <
171 60 µm in a Retsch MM400 mill with Zr grinding tools. 4.0 g of the sample powder were
172 mixed with 0.90 g of Licowax® C Micro-Powder PM (Fluxana, Germany), pressed into a 32
173 mm-pellet and analysed using an energy dispersive X-ray fluorescence spectrometer
174 (SPECTRO XEPOS, SPECTRO Analytical Instruments, Germany).
175 The $NH_4OAc$-EDTA extractable fractions (Cd, Cr, Cu, Ni, Pb, Zn, Al, Fe, Mn) were
176 measured according to Lakanen and Erviö (1971). Concentrations were determined by atomic
177 absorption spectroscopy using a graphite furnace and matrix modifiers.

178 After a pre-treatment of the samples with $H_2O_2$ (3%), particle size distribution of the soils was
179 measured using a combined method consisting of sieving the coarser particles (2000 - 32 µm)
180 and the measurement of the finer particles (< 32 µm) by means of an X-ray sedimentometer
181 (SediGraph 5100, Micromeretics, Norcross, GA, USA).
182
183 *Fractionation of organic matter*
184 Two different methods to characterise SOM were applied: a density fractionation and an
185 oxidation treatment using $H_2O_2$.
186 The density fractionation procedure was adapted from Christensen (1992). The following
187 fractions were separated: < 1 g/cm$^3$, 1-2 g/cm$^3$ and > 2 g/cm$^3$. Forty grams of fine earth were
188 added to 400 ml deionised water and stirred slightly. After about 12 h the sample was
189 centrifuged for 10 min at 5000 rpm. The supernatant (coarse particles) was sucked off and
190 evaporated (= density fraction < 1g/cm$^3$). The residual sample together with the suspended
191 material was dried at 40°C and subjected to a sodium polytungstate solution having a density
192 of 2 g/cm$^3$ to separate the 1-2 g/cm$^3$ fraction from the > 2g/cm$^3$ one. Ultrasonic treatment of
193 the density solution was done for 40 s at 50 J/ml and it was then centrifuged for 30 minutes at
194 3000 rpm. The supernatant having floating particles (density of 1.0 to 2.0 g/cm$^3$) was sucked
195 off and washed. To remove the salt, the sediment containing the associated mineral-SOM
196 fraction with $\rho$ > 2.0 g/cm$^3$ was washed three times using distilled water. Finally, the sample
197 was centrifuged and the supernatant was discarded. All fractions were dried at 40 °C.
198 Our conceptual approach was based, furthermore, on the finding that partial oxidative
199 degradation of OM leaves behind intrinsically resistant as well as mineral-protected organic
200 materials. The second method to characterise soil organic matter is based on the oxidation of
201 OM by 10% $H_2O_2$ (Eusterhues et al., 2005; Plante et al., 2004, modified). 1 gram of air-dried,
202 untreated soil (< 2mm) was wetted for 10 min with distilled water in a 250-ml beaker.
203 Afterwards, 90 ml of 10% $H_2O_2$ were added. The procedure was run at a temperature of 50 °C

throughout the treatment period. The beakers were closed by using two layers of parafilm to avoid evaporation of the reagent. Peroxide treatments were performed for 168h (7 days). At the end of the treatment the samples were washed three times with 40 ml deionised water and freeze-dried, their weights recorded, analysed for total C and N, and $^{14}C$ dated. The amount of organic C after the $H_2O_2$ treatment was related to the initial content using a mass-balance approach to obtain the corresponding recoveries with

$$(gC_{after} / gC_{before}) \times 100 \quad (1)$$

Recovery values were calculated also for nitrogen.

*Water-soluble phenolic materials*

Interest in phenolic material in soils relates to known or postulated involvement in allelopathy, metal translocation, as a marker of vegetative origin of soil organic matter (Lowe, 1993). Total water-soluble phenolic material can be obtained by colorimetric procedures based on the Folin-Ciocalteau reagent (Box, 1983). 5 g soil were shaken with 50 ml dist. water for 4 hours and then centrifuged (10000 rpm). 10 ml dist. water were added to a 10 ml aliquot of the filtered solution and subsequently 3 ml $Na_2CO_3$ solution followed by 1 ml Folin-Ciocalteau reagent. The phenol concentrations were measured with a spectrophotometer using a vanillic acid equivalent calibration curve.

*Mass balances*

Long-term weathering rates of soils were derived using immobile element contents (Brimhall and Dietrich, 1987; Chadwick et al., 1990; Egli and Fitze, 2000). Ti was used as an immobile element. Volumetric changes that occur during pedogenesis were determined by adopting the classical definition of strain, $\varepsilon_{i,W}$ (Brimhall and Dietrich, 1987):

$$\varepsilon_{i,W} = \frac{\Delta z_W}{\Delta z} - 1 \quad (2)$$

229 with $\Delta z$ as the columnar height (m) of a representative elementary volume of protore (or
230 unweathered parent material) $p$, and $\Delta z_W$ is the weathered equivalent height (m) $w$. With
231 respect to an immobile element, $\varepsilon_{i,W}$ can be calculated from (Chadwick et al., 1990):

232 $$\varepsilon_{i,w} = \left( \frac{\rho_p C_{i,p}}{\rho_w C_{i,w}} \right) - 1 \quad (3)$$

233 with $C_{i,p}$ (kg/t) as the concentration of the immobile element $i$ in the protolith (e.g.,
234 unweathered parent material, bedrock), $C_{i,W}$ as the concentration of immobile element $i$ in the
235 weathered product (kg/t) and $\rho_p$ and $\rho_W$ as the bulk density (t/m$^3$) of the protolith and the
236 weathered soil, respectively. The calculation of the open-system mass transport function $\tau_{j,w}$
237 is then defined by (Chadwick et al., 1990):

238 $$\tau_{j,W} = \left( \frac{\rho_W C_{j,W}}{\rho_p C_{j,p}} \left( \varepsilon_{i,W} + 1 \right) \right) - 1 \quad (4)$$

239 where $C_{j,p}$ (kg/t) is the concentration of element $j$ in protolith (e.g., unweathered parent
240 material, bedrock) and $C_{j,W}$ is the concentration of element $j$ in the weathered product (kg/t).
241 With $n$ soil layers, the calculation of changes in mass of element $j$ is given by (Egli and Fitze,
242 2000)

243 $$\bar{m}_{j,flux(z_w)} = \sum_{a=1}^{n} C_{j,p} \rho_p \left( \frac{1}{\varepsilon_{i,w} + 1} \right) \tau_{j,w} \Delta z_w \quad (5)$$

244 where $\tau_{j,w}$ corresponds to the mass transport function, $\varepsilon_{i,w}$ to the strain, and $\Delta z$ to the
245 weathered equivalent of the columnar height (m) of a representative elementary volume. The
246 units of mass fluxes are in kg/m$^2$.

247

248 *SEM and EDS analyses*

249 Selected treated and untreated soil samples were analysed using scanning electron microscopy
250 (SEM) and energy-dispersive spectroscopy (EDS). The samples were prepared for the SEM

analysis by first sonicating 10 µg of material for 30 s in 10 ml of deionised water and then transferring 60 µl of the solution onto standard aluminium Al-SEM stubs covered with aluminium foil. The analysis was performed using a Philips XL20 SEM operating at an accelerating voltage of 20 kV. Identification of minerals and organic matter was aided by the use of EDS which provides an elemental composition of the solid phases analysed. The EDS detector is equipped with an ultra-thin window allowing detection of mineral elements and carbon.

*Radiocarbon dating*

The $H_2O_2$ resistant carbon fraction was heated and catalytically reduced over cobalt powder at 550°C to elemental carbon (graphite). This mixture was pressed into a target and the ratios of $^{14}C$ to $^{12}C$ (for radiocarbon age) were measured by Accelerator Mass Spectrometry (AMS) using the tandem accelerator of the Institute for Particle Physics at the Swiss Federal Institute of Technology Zürich (ETH). The calendar ages were obtained using the OxCal 4.0.5 calibration program (Bronk Ramsey 1995, 2001) based on the IntCal 04 calibration curve (Reimer et al. 2004). Calibrated ages are given in the 2 $\sigma$ range (minimum and maximum value).

*Statistics*

As the data did not always show a normal distribution, correlation analysis was performed using the Pearson's correlation coefficient for normally distributed data and the Spearman's rank correlation coefficient for non-normally distributed ones (Sachs, 1992). A log-transformation of the data was necessary for the multiple regression analysis. Differences in mean values were tested with the U-test (Mann-Whitney). Both these procedures were checked by a two-sided test for significance.

277

278 **Results**

279

280 *Physical and chemical soil properties*

281 On north-facing sites, the soil profiles were classified (IUSS Working Group WRB, 2006) as
282 Entic, Umbric or Albic Podzols. On south-facing sites, the soils were Cambic Umbrisols on
283 paragneiss or Umbric Podzols on basaltic latite. All soils in the study area had a loam or
284 sandy-loam in the topsoils and a loamy-sand texture in the subsoil (Table 2). The acidification
285 of the soils developed on paragneiss (Val di Rabbi) was pronounced with pH-values in the
286 topsoil between 3.0 and 4.8 (Table 2), with the lowest values detected in the north-facing
287 soils. In contrast, the soils in Val di Fassa were slightly less acidified due to the latitic basalt
288 parent material, but also in this case the lower values were encountered in the north-facing
289 soils. Eluviation and illuviation of Fe and Al were in general more pronounced on north-
290 facing sites (Table 2). The mobilisation of SOM, however, was in most cases not intense
291 enough to produce absolute increases in the subsoil (Table 2).
292 The different lithology between Val di Rabbi (paragneiss) and Val di Fassa (latite) is reflected
293 by the main geochemical composition of the soil material (fine earth and soil skeleton; Table
294 3). The composition of the investigated parent materials primarily reflects the Si-rich and
295 granitic character for Val di Rabbi and the base cation-rich and latitic character for Val di
296 Fassa. Typically, latite had higher CaO, MgO, $Fe_2O_3$ and lower $SiO_2$ contents.
297 The total heavy metal concentrations did not differ greatly between the different lithologies.
298 except for Cu with higher concentrations in soils with latitic parent material (Table 3).
299 Relatively high concentrations of Cr were measured throughout all profiles. Pb was found in
300 elevated concentrations in the AE horizon of the Sorda 4 profile in Val di Fassa (122 mg/kg in
301 the fine earth, Table 4). According to the FOREGS (Forum of the European Geological
302 Surveys Directors) Geochemical Atlas (http://www.gtk.fi/publ/foregsatlas/; Salminen et al.,

303 2005), remote and almost unpolluted areas in Europe show a total Pb concentration in the
304 topsoil (0 – 20cm, with the organic layer removed) of approximately 10 – 18 mg Pb/kg and in
305 the subsoil of 6 – 15 mg Pb/kg. The Trentino region is in the southern Alps (Northern Italy)
306 and adjacent to the Po-valley – a highly industrialised and populated region (with the cities
307 Milan, Torin, Verona, Bologna, Venice etc.). Furthermore, the main north-south traffic axis
308 (the Brenner pass) crosses Trentino. Although the investigated sites are in remote areas, they
309 were to a certain extent influenced by human impact (emissions). The concentrations of Pb in
310 the parent material (fine earth) are low with about 8 – 23 mg Pb/kg (Median: 18.7 mg/kg;
311 Mean: 18.5 mg/kg). In the topsoil, however, total concentrations in the fine earth were
312 measured in the range of 31 – 122 mg Pb/kg (Median: 36 mg/kg; Mean: 45 mg/kg). These
313 values seem to be elevated when compared to the Pb-map of FOREGS. The median value in
314 Europe (according to the FOREGS Pb map) in the topsoil is 22.6 mg Pb/kg. This value is
315 distinctly lower than the one measured in the investigated soils. According to the Pb-map of
316 topsoils (FOREGS), around 33-42 mg Pb (total)/kg soil should be measured in the Trentino.
317 These are typical values found in areas with a certain human impact. Furthermore, the
318 FOREGS values fit quite nicely to our results. The median value (17.2 mg Pb/kg) in the
319 subsoils of Europe is, however, much closer to the values measured in the investigated
320 profiles (18.7 mg/kg).
321 The EDTA-extractable fraction (including the exchangeable fraction, organically-bound
322 species and species adsorbed onto oxyhydroxides; cf. McLaren and Crawford, 1973; Miller et
323 al., 1986; Keller and Védy, 1994; Zimmermann, 1997) of the trace metals decreased with
324 increasing soil depth (Table 4). The weakly-bound fraction of these metals (EDTA-
325 extractable) was often relatively low when compared to the total content. The dominant part
326 of the heavy metals was usually found in the strongly-bound fraction and only a very small
327 part was measured in the weakly-bound fraction, except for Pb and Cu. Up to 40% of the total
328 Pb amount was detected in the weakly bound fraction (predominantly in the topsoil) and up to

329 10% of Cu. The EDTA extractable content of Pb was partially very high and adverse effects
330 on microbial activity (Kabata-Pendias and Pendias, 2001) and soil fertility might be expected.
331 Also the EDTA-extractable amount of Cu reaches rather high values. The proportion of the
332 EDTA-extractable fraction is dependent on the pH for the elements Cr, Zn and Ni (with
333 higher values at a low pH). The EDTA-extractable heavy metals fraction can be in most cases
334 explained by the master variables pH, org. C content, oxyhydroxides (Feo) and the grain size
335 (clay content). The multiple regression analysis with respect to the individual heavy metals is
336 given in Table 5. Except for Cd and Zn, a significant part of the EDTA-extractable contents
337 could be explained by the chosen master variables.
338 The stocks of the EDTA-extractable heavy metals fraction is shown in Figure 1. The highest
339 amounts were measured for Pb and Cu. Except for Cu, a certain trend towards a higher
340 abundance of EDTA-extractable heavy metals on north-facing sites could be detected.
341
342 *Weathering losses*
343 The open-system mass transport functions $\tau$ are listed against depth for each soil and element
344 in Table 6. Generally, negative values and, thus, losses of the main elements were observed in
345 the topsoil. Mass transfer functions indicated losses of Na, Ca and Mg up to 70% in the AE,
346 E, or EA horizon. In general, the mass transfer function $\tau$ for the main elements is more
347 negative on north-facing sites which indicates a higher weathering intensity at such sites.
348 Heavy metals partially showed a different behaviour. Some trace elements (like Ni or Cu)
349 were leached from all investigated soils, others were often leached but also accumulated in
350 some cases (like Cr, Zn) while Pb was in all topsoils strongly accumulated (Table 6). Because
351 the Cd concentrations were often below the detection limit, the mass transport function could
352 not be calculated for this element.
353 In general, the $\tau$ values of Cu and Ni were lower on north-facing sites. This shows that these
354 elements are leached from the topsoil more intensively than on south-facing sites. Cr and Zn

355 showed an ambiguous behaviour. In several cases cases, the τ values were below 0 and in
356 others > 0 in the topsoil. Cr and Zn are, furthermore, more mobile in the soils on north-facing
357 sites lower because the τ values are lower there. In most cases, a distinct depletion of Cu, Zn
358 and Ni in the topsoil was measured. A part of the depleted heavy metals (e.g. Cu and Zn) was
359 accumulated in the subsoil indicating an active translocation process. In contrast, the Pb
360 concentrations in the soil profile exceed the concentrations of the lowest horizons and are
361 therefore distinctly higher than the lithogenic concentrations. A pronounced accumulation of
362 Pb is measured in the topsoils (with τ values in the range of about 1 – 12). This indicates an
363 enrichment that cannot only be explained by the chemical composition of the parent material.
364 Enrichment due to human impact is one possible source for the element Pb in the topsoil. The
365 Pb concentrations in the topsoil are often around 40 mg/kg and the τ values in the range of 0.4
366 – 2. At the site Sorda 4, Pb concentrations and the τ value are higher. Also other factors such
367 as site-specific characteristics might have contributed to a stronger accumulation of Pb. The τ
368 values for Pb were > 0 down to a considerable soil depth. This implies that also Pb is also
369 actively transported within the soil profile. The relatively high concentrations of Cr, Cu and
370 Ni in the soils of Val di Fassa were mostly due to the higher lithogenic content of these
371 elements. Cu, Cr, Ni and Zn were relatively intensively translocated within or leached from
372 the soil.
373
374 *Organic matter and density fractionation*
375 On north-facing sites, the SOC concentration in the soils (topsoil and also subsoil) is higher
376 than at the south-facing sites (Fig. 2): furthermore, a significant larger ($p < 0.01$) proportion of
377 carbon is stored in the light fraction (< 1g/cm$^3$, Table 7) on north-facing sites. The OM of the
378 light and intermediate density fraction is also found at greater depths on north-facing sites.
379 This indicates that more intense podzolisation processes on north-facing sites might have
380 favoured a deeper translocation of weakly decomposed, organic matter.

A large part of the soil organic carbon (SOC) was found in the heaviest fraction (Table 7). The amount of C in the fraction < 1 g/cm$^3$ decreased with soil depth as well as its proportion relative to the total SOC. In the fractions 1 – 2 g/cm$^3$ and especially > 2 g/cm$^3$ (Fig. 3), aggregates and organo-mineral associations protect organic material from decay (Sollins et al., 2006). The C/N ratio decreased from the light to the heavy fraction. The C/N ratio of the light fraction was very high which is typical for almost-undecomposed organic material (Table 7).

Water-soluble phenolic materials are usually measured in higher concentrations on north-facing sites (Table 2). Furthermore, phenols seem to penetrate into the soil more easily on north-facing sites although at all sites a distinct decrease between the surface layer (A, AE, OE, or E horizon) and the underlying B-horizon was measured.

*Labile and stable organic matter*

In the surface horizons, carbon recovery after oxidation by $H_2O_2$ was usually between 10 and 20% (range: 3 – 50 %). $H_2O_2$ was in general very effective in removing labile organic matter. The isolated pool of organic matter after the $H_2O_2$ treatment was found to be an inert fraction of SOM with a mixture of charcoal and almost polished surfaces where rests of organic material was strongly adsorbed on or trapped in (clay) minerals (Fig. 4). Highest recoveries were recorded in subsoils where less labile organic matter is present (Table 8). Compared to the untreated soils, the $H_2O_2$ treatment led to a relative enrichment of nitrogen (lower C/N ratios after the treatment). The recoveries of C were slightly lower at the north-facing sites (Table 8), which means that more labile organic matter could be oxidised at these sites.

The stable organic matter has very high ages. The $^{14}C$ ages of the $H_2O_2$-resistant fraction were up to 17000 years (Table 8).

## Discussion

*Weathering*

Eluviation and illuviation of Al and Fe within a soil profile were, independent of the parent material, more intense on north-facing slopes (Table 2). Mass transport functions ($\tau$) as well as absolute losses ($kg/m^2$; data not shown) for the major elements indicated a tendency towards higher weathering rates on north-facing sites compared to south-facing sites. These findings agree well with results from Hunckler and Schaetzl (1997). Although Alpine regions (in the subalpine to the alpine climate zone) have abundant precipitation, the availability of water and consequently the water fluxes in the soil play a decisive role in weathering and leaching of elements, organic matter and transformation of minerals (cf. Dambrine, 1986; Schaetzl and Isaard, 1996; Muhs et al., 2001). Evapotranspiration is lower at the cooler north-facing sites which gives rise to higher soil water fluxes. Several trace elements (Zn, Cu, Ni) also showed substantial weathering losses (Fig. 5). The comparison of EDTA-extractable Cr and Ni with the mass transport function of Al and Si (which can be considered as weathering indicators) evidenced a good correlation (better correlation for the first element). The higher the weathering intensity (of Al or Si), the more Cr and Ni is deliberated from minerals and crystal structures and transferred into a more easily extractable form. Zn, which is considered to be mobile in acid environments (Kabata Pendias and Pendias, 2001), correlated with the losses of the base cations while almost no relation to Si or Al could be found. The $\tau$ values of Cu, Cr, Ni and Zn showed a depletion in the topsoil and a corresponding accumulation, in some cases, in the subsoil. In the topsoil, the lithogenic contribution to the overall concentration in the fine earth was for Pb of minor importance (see also Blaser et al., 2000). No correlation between Pb and the weathering behaviour of Al, or Si (or any other major ions) could be detected. The $\tau$-values of Pb were strongly positive in the topsoil and indicated an accumulation (Table 6). The enrichment of lead in the topsoils can to a certain degree be

attributed to atmospheric input (Nowack et al., 2001; Blaser et al., 2000; Lévêque et al., 2002). The measured τ–value (10.53) for Pb in the topsoil (Table 6; site Sorda 4) is, however, very high when compared to similar investigations. In Swiss forest soils, for example, the maximum value for τ of Pb was near 5 (Blaser et al., 2000; there called "enrichment factor (EF)" which corresponds to EF = τ + 1). For some soils in the investigation area, the anthropogenic impact due to atmospheric pollution may be substantial. Specific site characteristics like the microclimate or erosion and accumulation processes, however, may also have contributed to the high value at Sorda 4. Temperature and precipitation have an important influence on the formation and decay rates of organic matter. According to Reimann et al. (2007b), many elements (Ag, Au, Bi, Cd, Hg, Pb, S, Sb, Se and Sr) show a strong enrichment in the O-horizon of soil profiles. These elements are taken up by plants and then returned to the O-horizon where they are strongly bound for varying lengths of time. The plants get rid of toxic or otherwise undesirable or no longer needed elements via litter fall. Relative enrichment also depends on the degree of humification and on the speed of decay of organic material, which is governed by climate, geology, topography and local conditions Reimann et al, 2007b).

In addition, the accumulated Pb is not only found in the uppermost layer. Pb seemed also to be transferred, either in the aqueous (less probable) or in the colloidal form (more probable), to greater soil depths. In a natural porous medium, strongly sorbing substances (like Pb, Cu or $Cr^{3+}$) are mainly associated with the solid phase, and consequently, the solution concentration of the substance in the pore water will be small (Grolimund et al., 1996; Carey et al., 2002). Since the solid phase is commonly assumed to be stationary, one usually surmises that such substances migrate very slowly in the subsurface. This conjecture has been challenged by the proposition that mobile, colloidal particles could act as pollutant carriers and thus provide a rapid transport pathway for strongly sorbing elements. In column experiments, Grolimund et al. (1996) showed that colloid-facilitated transport of Pb may be a dominant transport

459 pathway. In addition, Gasser et al. (1994) concluded from investigations of serpentinic soils
460 that colloid-mediated transport was an important pedogenetic process. They demonstrated,
461 inter alia, that coarse colloids in the soil water sampled from different soil horizons consisted
462 of primary minerals, together with secondary weathering products such as iron oxides and
463 organic matter. D'Amico et al. (2008) showed that Cu and Cr are transferred into greater soil
464 depths in podzols over ophiolitic materials. Other heavy metals are better soluble (e.g. Zn, Cd
465 or dichromate (having $Cr^{6+}$) or chromate anions) and are transferred relatively easily to
466 greater soil depths (e.g. Egli et al., 2006). Cr, Pb and also Zn were strongly accumulated in
467 the Bhs horizon in some other soils investigated in the Trentino region (Corradini and Sartori,
468 2004). In acid soils that are rich in organic matter, a downward movement of elements with a
469 very low solubility is very likely in colloidal form and/or metal-organic complexes.
470
471 *Organic matter*
472 The OC pools (fine earth) in the mineral horizons (A, E, B and BC horizons) were slightly
473 higher at the north-facing sites. On north-facing sites, a mean value of 21.3 $kg/m^2$ was
474 measured and on south-facing sites the value was 16.4 $kg/m^2$. The variability was, however,
475 relatively high (north-facing sites: SD = 7.9 $kg/m^2$; south-facing sites: SD = 7.4 $kg/m^2$).
476 Consequently, these differences were only significant at the 10% level (U-test).
477 In the investigated soils, the highest proportion of SOM was stored in the heavy fraction >
478 $2g/cm^3$. At the north-facing sites, in particular, a significant larger OM proportion is stored in
479 the light fraction (< 1 $g/cm^3$). The lightest fractions had a high C/N ratio due to the high
480 content of unaltered and undecomposed material (cf. Sollins et al., 2006; see also Fig. 3). This
481 means that degradation of organic matter has been more favoured on south-facing sites while
482 on north-facing sites more "labile" organic matter has been accumulated. When fractionated
483 according to density, the C/N ratio usually decreased with increasing particle density (Table
484 7; cf. Oades, 1989; Sollins et al., 2006; Basile-Doelsch et al., 2007). Sollins et al. (2006)

485 showed that C, N and lignin phenol concentrations all decreased and $^{14}C$ mean residence time
486 increased with particle density. The accumulation of poorly degraded organic matter on north-
487 facing sites is probably due to the scarcity of detrivore activity (that might be linked to the
488 higher water-soluble phenolic materials content; see Hättenschwiler and Vitousek, 2000) and,
489 generally, to the reduced microbial activity caused by higher soil acidity and lower
490 temperatures. Phenols may play an important role in humification. Phenolic compounds can
491 directly affect the composition and activity of decomposer communities and vice versa, thus
492 influencing the rates of decomposition and nutrient cycling (Hättenschwiler and Vitousek,
493 2000).
494 Similarly to the heavy density fraction, the stable organic C pool ($H_2O_2$-resistant fraction) was
495 enriched in N. This was most probably due to proteinaceous materials that adsorbed on
496 mineral surfaces (cf. Baldock et al., 2004; Kleber et al, 2007). The $H_2O_2$ left behind a fraction
497 which seems to be very stable and which is extremely old (Table 8). Kleber et al. (2007),
498 Kögel-Knabner et al. (2008) and others showed the importance of the mineral fraction in OM
499 protection. According to the model proposed by Kleber et al. (2007), the formation of
500 particularly strong organo-mineral associations appears to be favoured in the so-called
501 "contact zone" by situations where proteinaceous materials unfold upon adsorption, thus
502 increasing adhesive strength by adding hydrophobic interactions to electrostatic binding. The
503 amount of the $H_2O_2$-resistant fraction as well as the mean $^{14}C$ ages were lower in Val di Fassa
504 (latitic parent material). The soils in Val di Rabbi (paragneiss) had almost no earthworms
505 while in Val di Fassa the soil structures (Sartori and Chersich, 2007; Galvan et al., 2008)
506 revealed the presence of endogeic earthworms. We hypothesise that these organisms have
507 translocated some of the younger and less stable organic material (although tightly bound to
508 mineral surfaces) to greater soil depths which has led to a higher proportion of $H_2O_2$-
509 digestible carbon in the total organic C. The mean $^{14}C$ ages of the $H_2O_2$-resistant fraction were
510 in general higher on north-facing sites (9700 yr on north-facing sites and 6800 yr on south-

511 facing sites; Table 8). This could be due to less favourable degradation conditions and a lower
512 or almost missing macrofaunal activity on north-facing sites. A good correlation between the
513 C content in the $H_2O_2$-resistant fraction with the C content in the density fraction > 2 g/cm$^3$
514 was found (data not shown).
515 Precipitation and temperature particularly influence soil properties by affecting the type and
516 rates of chemical, biological and physical processes (Dahlgren et al., 1997; Birkeland, 1999).
517 Soil organic matter fractions, such as particulate organic matter (POM) or the light fraction,
518 have turnover times of years to decades and often respond more rapidly to management or
519 climate induced changes in the soil organic carbon pool than more stabilised, mineral-
520 associated fractions with longer turnover times (Gregorich and Janzen, 1996; Six et al., 1998;
521 Leifeld and Kögel-Knabner, 2005; Wagai et al., 2008). Light fraction and POM represent
522 plant and animal material at an early stage of decomposition (Christensen, 1996), it is a
523 transitional stage in the humification process. We showed that soil organic carbon contained
524 stable material with a very high radiocarbon age (up to 17000 years old), even though the
525 stabilisation processes leading to the formation of this old-soil carbon pool are not entirely
526 clear (Eusterhues et al., 2003; Helfrich et al., 2007).
527
528 *Interaction: heavy metals – organic and mineral-organic phases*
529 All investigated trace metals (EDTA-extractable form) were closely correlated with the water-
530 soluble phenolic materials. The highest correlation is obtained for Pb with $R = 0.86$ ($p <$
531 0.01), followed by Cu ($R = 0.74$; $p < 0.01$), Ni ($R = 0.64$; $p < 0.01$), Cd ($R = 0.61$; $p < 0.01$),
532 Zn ($R = 0.57$; $p < 0.01$) and Cr ($R = 0.53$; $p < 0.01$). All these metals seem, therefore, to have
533 a quite strong affinity to water-soluble phenolic materials. Although the statistical analyses
534 are not a proof, they indicate that the transport of these metals in the soil profile could have
535 been controlled, to a certain degree, by metal-organic (phenolic) complexes. Phenolic groups
536 are potential compounds that trap metals and enhance their translocation in soils (cf. Stumm

537 and Morgan, 1996). The organic stocks as well as the abundance of the light fraction and the
538 easily oxidisable organic matter fraction (Fig. 2) are higher on north-facing sites. Similarly,
539 but less significant, a slightly higher content of water-soluble phenolic materials can be
540 measured on north-facing sites. Lead was fixed in the light density fraction (< 1 g/cm$^3$), which
541 is more abundant in the topsoil, and also in the high (> 2 g/cm$^3$) density fraction (Fig. 6). A
542 considerable part of Pb was, therefore, bound to particulate organic matter which is easily
543 degradable and consequently may release (after oxidation or degradation) relatively easily Pb.
544 The major part of the element, however, seemed to be adsorbed onto or integrated into
545 organo-mineral complexes which are more stable than the fraction < 1 g/cm$^3$ (Sollins et al.,
546 2006). Similar to Pb, a part of Cu (and also Ni; data not shown) was incorporated into organo-
547 mineral complexes and, therefore, relatively tightly bound (Fig. 6). A similar information can
548 be obtained by comparing weakly bound heavy metals with the stable organic matter fraction
549 (Fig. 7). The EDTA-extractable Pb significantly correlated with the stable fraction ($R = 0.81$;
550 $p < 0.01$) and also with the labile soil organic matter fraction ($R = 0.60$; $p < 0.05$). The EDTA
551 extractable fractions of Ni and Cr are also correlated to the stable organic matter. Noteworthy
552 is the significant correlation of Cr with nitrogen of the stable fraction assuming a binding
553 mechanism with proteinaceous materials and mineral surfaces in the so-called “contact zone”
554 (Kleber et al., 2007).

555 High-mountain geo- and ecosystems are very sensitive to changing environmental conditions
556 such as global warming. The Alpine landscape responds noticeably and diversely to climate
557 change. As a consequence, landscape presently changes at very high rates (Haeberli et al.,
558 2007). Zanelli et al. (2006) showed that a fast and accelerating climate change has had a
559 remarkable influence on soil and humus chemistry even after only a few decades. Similarly,
560 Schmitt et al. (2008) reported dramatic changes of labile soil organic matter pools with
561 increased freeze-thaw cycles that were due to higher temperatures. In addition, Fissore et al.
562 (2008) indicated that soil organic matter quantity and quality may decrease in response to

563 global warming. A warmer climate could give rise to a change in microbiology with the
564 consequence that the weathering regime and SOM storage would be affected. We hypothesise
565 that global warming will lead to more favourable conditions in the soils at high elevations in
566 Alpine areas and consequently to an intensified biological activity in the short- to mid-term,
567 especially on north-facing slopes, and to an increase in SOM decomposition. As Pb and Cu
568 are related to the labile organic matter pools and the EDTA-extractable heavy metals to water-
569 soluble phenolic materials, the risk exists that the heavy metals storage capacity and mobility
570 in soils could also change.
571
572 **Conclusions**
573
574 Alpine sites near the timberline are characterised by extreme climatic conditions. Exposure
575 and thus climate influence not only weathering losses but also humus properties and
576 chemistry and consequently also the behaviour of heavy metals. Our principal findings are:
577 - The open-system mass transport functions showed high losses of the major elements.
578 Some of the investigated heavy metal concentration profiles (Cr, Ni) were directly related
579 to weathering, while Pb is enriched and partially linked to atmospheric deposition. Human
580 impact and in some cases a relative enrichment due to humification and site-specific
581 characteristics have contributed to the accumulation of Pb.
582 - Weathering losses of major cations as well as of some heavy metals (Cr, Zn, Cu, Ni) are in
583 general higher at the north-facing sites.
584 - The OC pools are slightly higher at the north-facing sites.
585 - A significant part of the organic matter in the investigated sites occurred in an easily-
586 degradable form (fraction < 1 g/cm$^3$ or the $H_2O_2$-oxidisable fraction). A higher amount
587 and proportion was found at the north-facing sites. More labile organic matter
588 accumulated at the cooler northern sites due to reduced microbial activity. This was

caused by a high soil acidity and low summer temperatures. Lead and copper correlated to the light fraction (< 1 g/cm$^3$) and the $H_2O_2$-oxidisable, labile organic fraction and, even more significant, also to the heavy (> 2 g/cm$^3$) and the stable ($H_2O_2$-resistant) fraction. The other metals had a significant affinity only to the stable (and heavy) organic fraction.

- The abundance (stocks) of the EDTA-extractable fraction (including the exchangeable fraction of organically-bound species and species adsorbed on to oxyhydroxides) of heavy metals was, in most cases, higher on north-facing sites. Large fractions of Pb and Cu were found to be EDTA extractable (up to 40%; Table 4, Fig. 1). All other elements occur predominantly in the stronger bound fraction (e.g. silicatic fraction).
- All heavy metals (EDTA-extractable form) correlated well with the water-soluble phenolic materials concentration. Pb and Cu are, furthermore, significantly related to the labile organic matter pools. A possible future change in SOM (due to global warming) would probably affect the water-soluble phenolic materials and the labile organic matter pool and consequently also the storage capacity and mobility of heavy metals. We can assume that especially the EDTA-extractable heavy metals stocks could be affected (Fig. 1). The type and speed of changes are, however, completely unknown as yet.

**Acknowledgements**

We would like to express our appreciation to B. Kägi for his assistance in the laboratory. This research was supported by a grant from the Ministero delle Politiche Agricole e Forestali (Roma, Italia; project: MEPESA). We are, furthermore, indebted to three unknown reviewers for their helpful comments on an earlier version of the manuscript.

**References**

615 April R, Newton R, Truettner Coles L. Chemical weathering in two Adirondack watersheds:
616 past and present-day rates. Geol Soc Am Bull 1986; 97: 1232-1238.
617 Bain DC, Mellor A, Wilson MJ, Duthie DML. Chemical and mineralogical weathering rates
618 and processes in an upland granitic till catchment in Scotland. Water Air Soil Poll 1994;
619 73: 11-27.
620 Baldock JA, Masiello CA, Gélinas Y, Hedges JI. Cycling and composition of organic matter
621 in terrestrial and marine ecosystems. Marine Chem 2004; 92: 39-64.
622 Basile-Doelsch I, Amundson R, Stone WEE, Borschneck D, Bottero JY, Moustier S, Masin F,
623 Colin F. Mineral control of carbon pools in a volcanic soil horizon. Geoderma 2007; 137:
624 477-489.
625 Bindler R, Branvall ML, Renberg I, Emteryd O, Grip H. Natural lead concentrations in
626 pristine boreal forest soils and past pollution trends: A reference for critical load models.
627 Env Sci Technol 1999; 33; 3362–3367.
628 Birkeland PW. Soils and geomorphology. Oxford University Press, New York, 1999.
629 Blaser P, Zimmermann S, Luster J, Shotyk W. Critical examination of trace element
630 enrichments and depletions in soils: As, Cr, Cu, Ni, Pb, and Zn in Swiss forest soils. Sci of
631 Total Environ 2000; 249: 257-280.
632 Box JD. Investigation of the Folin-Ciocalteau phenol reagent for the determination of
633 polyphenolic substances in natural waters. Water Res 1983; 17: 511-525.
634 Bowen HJM. Environmental chemistry of the elements. Academic Press, New York, 1979.
635 Brimhall GH, Dietrich WE. Constitutive mass balance relations between chemical
636 composition, volume, density, porosity, and strain in metasomatic hydrochemical systems:
637 results on weathering and pedogenesis. Geochim Cosmochim Acta 1987; 51: 567-587.
638 Bronk Ramsey C. Radiocarbon calibration and analysis of stratigraphy: The OxCal program.
639 Radiocarbon 1995; 37: 425-430.

640 Bronk Ramsey C. Development of the radiocarbon calibration program OxCal. Radiocarbon
641 2001; 43: 355-363.
642 Carey PL, Bidwell VJ, McLaren RG. Chromium(VI) leaching from large undisturbed soil
643 lysimeters following application of a simulated copper-chromium-arsenic (CCA) timber
644 preservative. Austr J Soil Res 2002; 40: 351-365.
645 Chadwick OA, Brimhall GH, Hendricks DM. From a black to a gray box – a mass balance
646 interpretation of pedogenesis. Geomorphology 1990; 3: 369-390.
647 Christensen BT. Physical fractionation of soil and organic matter in primary particle size and
648 density separates. Adv Agron 1992; 20: 1–90.
649 Christensen BT. Matching measurable soil organic matter fractions with conceptual pools in
650 simulation models of carbon turnover: revision of model structure. In: Smith JU, editor.
651 Evaluation of Soil Organic Matter Models. Springer, Berlin, 1996, pp. 143–160.
652 Corradini F, Sartori G. Soil and water chemistry in two forest sites of Trentino (Italian Alps).
653 Studi Trent Sci Nat Acta Biol 2004; 81, Suppl. 1: 153-164.
654 Dahlgren RA, Boettinger JL, Huntington GL, Amundson RG. Soil development along an
655 elevational transect in the western Sierra Nevada, California. Geoderma 1997; 78: 207-
656 236.
657 Dambrine E. Répartition, morphologie et fonctionnnement des Podzols de haute montagne
658 crystalline sous climat tempéré. In: Righi D, Chauvel A, editors, Podzols et Podzolisation,
659 Institut National de la Recherche Agronomique, (INRA) et AFES, Paris, 1986, pp. 69-83.
660 D'Amico M, Julitta F, Previtali F, Cantelli D. Podzolization over ophiolitic materials in the
661 western Alps (Natural Park of Mont Avic, Aosta Valley, Italy). Geoderma 2008; 146: 129-
662 137.
663 Eggenberger U. Mineral weathering in soils: experiments, field studies, and modeling. Ph.D.
664 Thesis, University of Berne, Switzerland, 1995.

665 Egli M, Fitze P. Formulation of pedologic mass balance based on immobile elements: a
666 revision. Soil Sci 2000; 165: 437-443.
667 Egli M, Mirabella A, Sartori G, Fitze P. Weathering rates as a function of climate: results
668 from a climosequence of the Val Genova (Trentino, Italian Alps). Geoderma 2003; 111:
669 99-121.
670 Egli M, Mirabella A, Kägi B, Tomasone R., Colorio G. Influence of steam sterilisation of
671 soils on organic matter, soil chemical characteristics, heavy metals and clay mineralogy.
672 Geoderma 2006; 131: 123-142.
673 Egli M, Mirabella A, Sartori G. The role of climate and vegetation in weathering and clay
674 mineral formation in late Quaternary soils of the Swiss and Italian Alps. Geomorphology
675 2008; 102: 307-324.
676 Eusterhues K, Rumpel C, Kleber M, Kögel-Knabner I. Stabilization of soil organic matter by
677 interactions with minerals as revealed by mineral dissolution and oxidative degradation.
678 Org Geochem 2003; 34: 1591-1600.
679 Eusterhues K, Rumpel C, Kögel-Knabner I. Stabilization of soil organic matter isolated via
680 oxidative degradation. Org Geochem 2005; 36: 1567-1575.
681 FAO (Food and Agriculture Organization of the United Nations). World Reference Base for
682 Soil Resources. World Soil Resources Reports 84, FAO, Rome, 1998.
683 Favilli F, Egli M, Brandová D, Ivy-Ochs S, Kubik PW, Cherubini P, Mirabella A, Sartori G,
684 Giaccai D, Haeberli W. Combined use of relative and absolute dating techniques for
685 detecting signals of Alpine landscape evolution during the late Pleistocene and early
686 Holocene. Geomorphology 2009; 112, 48-66.
687 Fissore C, Giardina CP, Kolka RK, Trettin CC, King GM, Jurgensen MF, Barton CD,
688 Mcdowell SD. Temperature and vegetation effects on soil organic carbon quality along a
689 forested mean annual temperature gradient in North America. Global Change Biol 2008;
690 14: 193-205.

691 Galvan P, Ponge JF, Chersich S, Zanella A, Humus components and soil biogenic structures
692 in Norway spruce ecosystems. Soil Sci Soc Am J 2008; 72: 548-557.
693 Gasser UG, Juchler SJ, Sticher H. Chemistry and speciation of soil water from serpentinic
694 soils: importance of colloids in the transport of Cr, Fe, Mg, and Ni. Soil Sci 1994; 158:
695 314-322.
696 Gasser UG, Juchler SJ, Hobson WA, Sticher H. The fate of chromium and nickel in sub-
697 alpine soils derived from serpentinite. Can J Soil Sci 1995; 75: 187-195.
698 Green EG, Dietrich WE, Banfield JF.. Quantification of chemical weathering rates across an
699 actively eroding hillslope. Earth Planet Sci Lett 2006; 242: 155-169.
700 Gregorich EG, Janzen HH.. Storage of soil carbon in the light fraction and macroorganic
701 matter. In: Carter MR, Stewart BA, editors. Advances in Soil Science —Structure and
702 Organic Matter Storage in Agricultural Soils. Lewis Publishers, New York, 1996, pp. 167–
703 190.
704 Grolimund D, Borkovec M, Barmettler K, Sticher H. Colloid-facilitated transport of strongly
705 sorbing contaminants in natural porous media: a laboratory column study. Env Sci
706 Technol 1996; 30: 3118-3123.
707 Haeberli W, Keller F, Krüsi B, Egli M, Rothenbühler C, Meilwes J, Gruber S. Raum-zeitliche
708 Informationen über schnelle Klimaänderungen in hochalpinen Umweltsystemen als
709 strategisches Werkzeug für Analyse, Kommunikation, partizipative Planung und
710 Management im Tourismusgebiet Oberengadin. Schlussbericht GISALP, NFP48
711 (Nationales Forschungsprogramm „Alpen“). vdf-Verlag, Zürich, 2007
712 Hättenschwiler S, Vitousek PM. The role of polyphenols in terrestrial ecosystem nutrient
713 cycling. Tree 2000; 15: 238-243.
714 Helfrich M, Flessa H, Mikutta R, Dreves A, Ludwig B. Comparison of chemical
715 fractionations methods for isolating stable soil organic carbon pools. Europ J Soil Sci
716 2007; 58: 1316-1329.

717 Hitz C, Egli M, Fitze P. Determination of the sampling volume for representative analysis of
718 alpine soils. Z Pflanzenernähr Bodenkd 2002; 165: 326-331.
719 Hossner CR. Dissolution for total elemental analysis. In: Sparks DL, editor. Methods of Soil
720 Analysis, Part 3 Chemical Methods, Soil Science Society of America Inc. and American
721 Society of Agronomy Inc., Madison, Wisconsin, 1996, pp. 49-64.
722 Hunckler RV, Schaetzl RJ. Spodosol development as affected by geomorphic aspect, Baraga
723 County, Michigan. Soil Sci Soc Am J 1997; 61: 1105-1115.
724 IUSS Working Group WRB. World Reference Base for Soil Resources 2006, 2nd edition,
725 World Soil Resources Reports No. 103, FAO (Food and Agriculture Organisation of the
726 United Nations), Rome, 2006.
727 Kabata Pendias A, Pendias H. Trace elements in soils and plants. CRC Press, London, 2001.
728 Keller C, Védy J-C. Distribution of copper and cadmium fractions in two forest soils. J
729 Environl Qual 1994; 23: 987-999.
730 Kleber M, Sollins P, Sutton R. A conceptual model of organo-mineral interactions in soils:
731 self-assembly of organic molecular fragments into zonal structures on mineral surfaces.
732 Biogeochem 2007; 85: 9-24.
733 Kögel-Knabner I, Guggenberger G, Kleber M, Kandeler E, Kalbitz K, Scheu S, Eusterhues K,
734 Leinweber P. Organo-mineral associations in temperate soils: Integrating biology,
735 mineralogy, and organic matter chemistry. J Plant Nutr Soil Sci 2008; 171: 61-82.
736 Lakanen E, Erviö R. A comparison of eight extractants for the determination of plant-
737 available micronutrients in soil. Acta Agralia Fennica 1971; 123: 223 – 235.
738 Langley-Turnbaugh SJ, Bockheim JG. Mass balance of soil evolution on late Quaternary
739 marine terraces in coastal Oregon. Geoderma 1998; 84: 265-288.
740 Leidlmair A. Tirol-Atlas. Eine Landeskunde in Karten,Tiroler Landesregierung –
741 Kulturreferat, Alpina Offset, Innsbruck, 1996.
742 Leifeld J, Kögel-Knabner I. Soil organic matter fractions as early indicators for carbon stock

743 changes under different land-use? Geoderma 2005; 124: 143-155.
744 Lévêque J, Philippe S, Baize D, Monna F, Haack U. Utilisation des isotopes stables pour la
745 détermination de l'origine (géogene ou industrielle) du plomb. In: Baize D, Tercé M,
746 editors. Les éléments traces métalliques dans les sols. INRA, Paris, 2002, pp. 375-391.
747 Lowe LE. Water-soluble phenolic materials. In: Carter MR, editor. Soil Sampling and
748 Methods of Analysis, Canadian Society of Soil Science, Lewis Publishers, 1993, pp. 409-
749 412.
750 McKeague JA, Brydon JE, Miles NM. Differentiation of forms of extractable iron and
751 aluminium in soils. Soil Sci Soc Am Proc 1971; 35: 33-38.
752 McLaren RG, Crawford DV. Studies on soil copper: I. the fractionation of copper in soil. J.
753 Soil Sci 1973; 24,:173-181.
754 Miller WP, Martens DC. Zelazny LW. Effect of sequence in extraction of trace metals from
755 soils. Soil Sci Soc Am J 1986; 50: 598-601.
756 Muhs DR, Bettis EA, Been J, McGeehin JP. Impact of climate and parent material on
757 chemical weathering in loess-derived soils of the Mississippi river valley. Soil Sci Soc Am
758 J 2001; 65: 1761-1777.
759 Nowack B, Obrecht J-M, Schluep M, Schulin R, Hansmann W, Köppel V. Elevated lead and
760 zinc contents in remote Alpine soils of the Swiss Natural Park. J Env Qual 2001; 30: 919-
761 926.
762 Oades JM. An introduction to organic matter in mineral soils. In: Dixon JB, Weed SB,
763 editors. Minerals in Soil Environments, Second ed. Soil Science Society of America,
764 Madison, WI, 1989, pp. 89–159.
765 Plante AF, Chenu C, Balabane M, Mariotti A, Righi D. Peroxide oxidation of clay-associated
766 organic matter in a cultivation chronosequence. Europ J Soil Sci 2004; 55: 471-478.
767 Reimann C, de Caritat P. Intrinsic flaws of element enrichment factors (EFs) in environmental
768 geochemistry. Env Sci Tech 2000; 34: 5084-5091.

769 Reimann C, de Caritat P. Distinguishing between natural and anthropogenic sources for
770 elements in the environment: regional geochemical surveys versus enrichment factors. Sci
771 of Total Environ 2005; 337: 91-107.
772 Reimann C, Arnoldussen A, Finne TE, Koller F, Nordgulen Ø. Englmaier P. Element
773 contents in mountain birch leaves, bark and wood under different anthropogenic and
774 geogenic conditions. Appl Geochem 2007a; 22: 1549-1566.
775 Reimann C, Arnoldussen A, Englmaier P, Filzmoser P, Finne TE, Garrett RG, Koller F,
776 Nordgulen Ø. Element concentrations and variations along a 120-km transect in southern
777 Norway – Anthropogenic vs. geogenic vs. biogenic element sources and cycles. Appl
778 Geochem 2007b; 22: 851-871.
779 Reimer PJ, Baillie MGL, Bard E, Bayliss A, Beck JW, Bertrand CJH, Blackwell PG, Buck
780 CE, Burr GS, Cutler KB, Damon PE, Edwards RL, Fairbanks RG, Friedrich M, Guilderson
781 TP, Hogg AG, Hughen KA, Kromer B, McCormac G, Manning S, Bronk Ramsey C,
782 Reimer RW, Remmele S, Southon JR, Stuiver M, Talamo S, Taylor FW, van der Plicht J,
783 Weyhenmeyer CE. IntCal04 terrestrial radiocarbon age calibration, 0-26 cal kyr BP.
784 Radiocarbon 2004; 46: 1029-1058.
785 Richter DD, Hofmockel M, Callaham MA, Powlson DS, Smith P. Long-term soil
786 experiments: Keys to managing Earth's rapidly changing ecosystem. Soil Sci Soc Am J
787 2007; 71: 266-279.
788 Riebe CS, Kirchner JW, Finkel RC. Erosional and climatic effects on long-term chemical
789 weathering rates in granitic landscapes spanning diverse climate regimes. Earth Planet Sci
790 Lett 2004a; 224: 547-562.
791 Riebe CS, Kirchner JW, Finkel RC, Sharp decrease in long-term chemical weathering rates
792 along an altitudinal transect. Earth Planet Sci Lett 2004b; 218: 421-434.
793 Rosman KJR, Chisholm W, Boutron CF, Candelone JP, Gorlach U. Isotopic evidence for the
794 source of lead in Greenland snows since the late 1960s. Nature 1993; 362: 333–335.

795 Sachs L. Angewandte Statistik. Anwendung statistischer Methoden. Siebte Auflage, Springer-
796 Verlag, Berlin,1992.
797 Salminen R (Chief-editor), Batista MJ, Bidovec M, Demetriades A, De Vivo B, De Vos W,
798 Duris M, Gilucis A, Gregorauskiene V, Halamic J, Heitzmann P, Lima A, Jordan G,
799 Klaver G, Klein P, Lis J, Locutura J, Marsina K, Mazreku A, O'Connor PJ, Olsson SÅ,
800 Ottesen R-T, Petersell V, Plant JA, Reeder S, Salpeteur I, Sandström H, Siewers U,
801 Steenfelt A, Tarvainen T. Geochemical Atlas of Europe. Part 1: Background Information,
802 Methodology and Maps. Espoo, Geological Survey of Finland, 526 p., 2005.
803 Salvador-Blanes S, Cornu S, Bourennane H, King D. Controls of the spatial variability of Cr
804 concentration in topsoils of a central French landscape. Geoderma 2006; 132: 143-157.
805 Sartori G, Chersich S. I suoli della Piana delle Viote. Paesaggi, suoli e forme di humus.
806 Report n. 39, Centro di Ecologia Alpina, Trento, Italy, 2007.
807 Schaetzl RJ, Isard SA. Regional-scale relationships between climate and strength of
808 podzolization in the Great Lakes Region, North America. Catena 1996; 28: 47-69.
809 Schmitt A, Glaser B, Borken W, Matzner E. Repeated freeze-thaw cycles changed organic
810 matter quality in a temperate forest soil. J Plant Nutr Soil Sci 2008; 171: 707-718.
811 Six J, Elliott ET, Paustian K, Doran JW. Aggregation and soil organic matter accumulation in
812 cultivated and native grassland soils. Soil Sci Soc Am J 1998; 63: 1350–1358.
813 Soil Survey Staff. Keys to Soil Taxonomy, 10th ed. USDA-Natural Resources Conservation
814 Service, Washington, DC, 2006.
815 Sollins P, Swanston C, Kleber M, Filley T, Kramer M, Crow S, Caldwell BA, Lajtha K,
816 Bowden R. Organic C and N stabilization in a forest soil: Evidence from sequential density
817 fractionation. Soil Biol Biochem 2006; 38: 3313-3324.
818 Stiles CA, Mora CI, Driesse SG. Pedogenetic processes and domain boundaries in a Vertisol
819 climosequence: evidence from titanium and zirconium distribution and morphology.
820 Geoderma 2003; 116: 279–299.

821 Stumm W, Morgan JJ. Aquatic chemistry. Third edition. John Wiley and Sons, Inc., New
822 York, 1996.
823 Wagai R, Mayer LM, Kitayama K, Knicker H. Climate and parent material controls on
824 organic matter storage in surface soils: A three-pool, density-separation approach.
825 Geoderma 2008; 147: 23-33.
826 Weiss D, Shotyk W, Appleby PG, Kramers JD, Cheburkin AK. Atmospheric Pb deposition
827 since the industrial revolution recorded by five Swiss peat profiles: Enrichment factors,
828 fluxes, isotopic composition, and sources. Env Sci Technol 1999; 33: 1340–1352.
829 White AF, Blum AE. Effects of climate on chemical weathering in watersheds. Geochim
830 Cosmochim Acta 1995; 59: 1729-1747.
831 Zanelli R, Egli M, Fitze P, Giaccai D, Mirabella A. Influence of laurophyllous species,
832 chestnut and native vegetation on organic matter in soils in Southern Switzerland and
833 Northern Italy. Geoderma 2006; 136: 723-737.
834 Zimmermann KS. Wirkung einer gepufferten Ammonium-Acetat-EDTA-Extraktion auf aus-
835 gewählte Bodenbestandteile und natürliche Bodenproben. Diss. ETH Nr. 12134, Zürich,
836 1997.

**Table 1**
**Click here to download Table: Table1.doc**

Table 1. Characteristics of the study sites in Val di Rabbi and Val di Fassa – Southern Alps.

| Profile | Valley | Coordinates (N/E) | Elevation (m asl) | Aspect (°N) | Slope (°) | MAT[1] (°C) | MAP[1] (mm/y) | Parent material | Vegetation | Land use[2] | WRB (IUSS Working Group WRB, 2006) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| South-facing sites | | | | | | | | | | | |
| S6 | Val di Rabbi | 46°22.3'/ 10°53.0' | 1660 | 210 | 33 | 4.0 | 1050 | Paragneiss debris | Larici-Piceetum | Natural forest (ecological forestry) | Cambic Umbrisol (Episkeletic) |
| S7 | Val di Rabbi | 46°20.7'/ 10°52.1' | 1995 | 160 | 25 | 2.1 | 1160 | Paragneiss debris | Laricetum | Ex-pasture, natural forest | Cambic Umbrisol (Episkeletic) |
| Sorda 1 | Val di Fassa | 46°23.3'/ 11°33.7' | 1620 | 165 | 35 | 4.2 | 1100 | Basaltic latite debris | Piceetum | Natural forest (ecological forestry) | Umbric Podzol (Episkeletic) |
| S. Nicolò 4 | Val di Fassa | 46°26.3'/ 11°41.7' | 1915 | 195 | 33 | 2.5 | 1200 | Basaltic latite debris | Piceetum | Natural forest (ecological forestry) | Umbric Podzol (Endoskeletic) |
| North-facing sites | | | | | | | | | | | |
| N2 | Val di Rabbi | 46°24.1'/ 10°48.1' | 1620 | 0 | 29 | 4.2 | 1040 | Paragneiss debris | Piceetum | Natural forest (ecological forestry) | Entic Podzol (Endoskeletic) |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| N3 | Val di Rabbi | 46°22.8'/ 10°47.0' | 1930 | 20 | 12 | 2.5 | 1140 | Paragneiss debris and glacial material | Nardetum alpigenum | Pasture | Albic Podzol (Episkeletic) |
| Sorda 4 | Val di Fassa | 46°23.0'/ 11°32.3' | 1640 | 350 | 36 | 4.1 | 1100 | Basaltic latite debris | Piceetum | Natural forest (ecological forestry) | Umbric Podzol (Endoskeletic) |
| S. Nicolò 2 | Val di Fassa | 46°27.2'/ 11°40.7' | 1920 | 300 | 29 | 2.5 | 1200 | Basaltic latite debris | Piceetum | Natural forest (ecological forestry) | Entic Podzol (Endoskeletic) |

[1] MAT = mean annual temperature, MAP = mean annual precipitation (according to Leidlmair, 1996).
[2] Ecological forestry: silvicultural and management techniques mimic ecological processes. This includes a) no clear-cutting, b) forestry is implemented at the stand scale, c) single tree cutting, d) promotion of diverse and healthy forests across the landscape.

**Table 2**
**Click here to download Table: Table2.doc**

Table 2. Some physical and chemical properties of the investigated soils in Val di Rabbi and Val di Fassa.

| Exposure/ valley, site | Horizon | Depth (cm) | Munsell color (moist) | Skeleton w-% | Density g/cm$^3$ | Sand[1] g/kg | Silt g/kg | Clay g/kg | pH ($CaCl_2$) | org. C g/kg | N g/kg | Phenols[2] mg/kg | $Al_o$ g/kg | $Fe_o$ g/kg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| South-facing | | | | | | | | | | | | | | |
| Val di Rabbi | | | | | | | | | | | | | | |
| S6 | AE | 3-10 | 10YR 4/4 | 16 | 0.82 | 490 | 370 | 140 | 4.2 | 49.3 | 2.06 | 63.91 | 8.6 | 8.1 |
| | Bs1 | 10-50 | 10YR 4/4 | 24 | 1.13 | 495 | 400 | 105 | 4.4 | 38.1 | 1.51 | 17.62 | 8.4 | 6.6 |
| | Bs2 | 50-90 | 10YR 4/4 | 50 | 1.24 | 595 | 375 | 30 | 4.6 | 16.6 | 0.77 | 5.94 | 8.8 | 4.6 |
| | BC | 90-125 | 10YR 4/3 | 69 | 1.35 | 797 | 175 | 28 | 4.6 | 12.9 | 0.52 | 6.18 | 4.3 | 2.8 |
| S7 | AE | 0-10 | 7.5 YR 3/2 | 1 | 0.7 | 415 | 370 | 215 | 4.0 | 85.9 | 5.34 | 62.08 | 7.3 | 9.3 |
| | BA | 10-30 | 7.5 YR 2.5/2 | 42 | 1.42 | 375 | 520 | 105 | 4.4 | 64.5 | 3.42 | 9.52 | n.m. | n.m. |
| | Bs1 | 30-45 | 7.5 YR 3/4 | 42 | 1.42 | 642 | 314 | 44 | 4.6 | 15.9 | 0.48 | 5.34 | 8.7 | 3.2 |
| | Bs2 | 45-70 | 10 YR 4/4 | 33 | 1.61 | 810 | 176 | 14 | 4.8 | 8.7 | 0.27 | 3.75 | 8.2 | 2.8 |
| | BC | 70-95 | 2.5 YR 4/3 | n.m. | n.m. | 690 | 295 | 15 | 4.8 | 3.8 | 0.16 | 2.35 | n.m. | n.m. |
| | C | 95-110 | 2.5 YR 5/4 | 42 | 1.8 | 500 | 475 | 25 | 4.8 | 3.0 | n.d. | 2.43 | 2.6 | 0.8 |
| Val di Fassa | | | | | | | | | | | | | | |
| Sorda 1 | A | 2-10 | 10YR 2/2 | 55 | 0.87 | 710 | 170 | 120 | 5.0 | 45.9 | 2.20 | 141.13 | 6.3 | 5.7 |
| | BA | 20-37 | 7.5YR 2.5/2 | 63 | 1.01 | 560 | 230 | 210 | 5.3 | 24.4 | 1.40 | 31.79 | 9.4 | 7.4 |
| | Bs | 37-55 | 7.5YR 3/3 | 84 | 1.18 | 720 | 200 | 79 | 5.4 | 20.9 | 1.50 | 25.49 | 16.1 | 9.9 |
| | CB | 55-80 | 7.5YR 2.5/1 | 74 | 1.35 | 880 | 94 | 26 | 5.7 | 6.4 | 0.60 | 9.18 | 7.0 | 5.5 |
| S. Nicolò 4 | AE | 4-12 | 7.5YR 3/2 | 44 | 0.77 | 590 | 250 | 160 | 4.8 | 77.3 | 5.00 | 102.72 | 11.7 | 10.5 |
| | BA | 12-28 | 7.5YR 2.5/2 | 39 | 0.77 | 610 | 240 | 150 | 5.1 | 50.6 | 3.70 | 60.89 | 13.8 | 12.8 |
| | Bs1 | 28-50 | 5YR 3/3 | 42 | 0.86 | 580 | 260 | 160 | 5.3 | 26.2 | 2.00 | 27.91 | 15.4 | 16.5 |
| | Bs2 | 50-82 | 7.5YR 4/4 | 27 | 0.82 | 640 | 260 | 100 | 5.5 | 20.3 | 1.50 | 25.14 | 13.9 | 14.8 |
| | BC1 | 82-120 | 7.5YR 4/3 | 38 | 0.89 | 720 | 194 | 86 | 5.5 | 3.5 | 0.40 | 14.62 | 5.8 | 10.3 |
| | BC2 | >120 | 10YR 4/3 | 49 | 1.19 | n.m. | n.m. | n.m. | n.m. | n.m. | n.m. | 7.78 | n.m. | n.m. |
| North-facing | | | | | | | | | | | | | | |
| Val di Rabbi | | | | | | | | | | | | | | |
| N2 | E | 6-12 | 7.5YR 3/1 | 35 | 0.96 | 360 | 480 | 160 | 3.0 | 56.5 | 2.47 | 104.18 | 3.1 | 6.6 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Bs1 | 12-50 | 7.5YR 4/6 | 67 | 1.21 | 400 | 525 | 75 | 4.2 | 23.1 | 0.83 | 23.08 | 5.8 | 9.5 |
| | Bs2 | 50-100 | 7.5YR 4/6 | 80 | 1.46 | 625 | 325 | 50 | 4.6 | 16.0 | 0.63 | 13.75 | 11.1 | 13.2 |
| | BC | 100-130 | 10YR 4/6 | n.m. | n.m. | 751 | 220 | 29 | 4.7 | 4.4 | 0.19 | 2.76 | n.m. | n.m. |
| | C | 130-150 | 10YR 5/4 | 60 | 1.71 | n.m. | n.m. | n.m. | 4.7 | 2.7 | 0.07 | 1.86 | 2.1 | 2.5 |
| N3 | EA | 1-10 | 7.5YR 2.5/1.5 | 0 | 0.63 | 380 | 440 | 180 | 3.9 | 194.2 | 11.17 | 58.12 | 9.7 | 11.6 |
| | E | 10-12 | 7.5YR 4/1 | 0 | 0.63 | 518 | 336 | 146 | 3.9 | 82.0 | 3.61 | 18.66 | n.m. | n.m. |
| | Bhs | 12-25 | 5YR 2.5/1 | 29 | 1.13 | 509 | 366 | 125 | 4.0 | 66.4 | 2.70 | 15.13 | 13.5 | 20.2 |
| | Bs | 25-57 | 2.5YR 3/2 | 43 | 1.13 | 619 | 322 | 59 | 4.3 | 28.0 | 1.01 | 6.51 | 14.5 | 12.5 |
| | BC | 57-80 | 10YR 4/3 | n.m. | n.m. | 746 | 219 | 35 | 4.5 | 10.1 | 0.49 | 3.65 | n.m. | n.m. |
| | C | 80-110 | 10YR 5/4 | 63 | 1.77 | 756 | 210 | 34 | 4.5 | 7.2 | 0.25 | 2.55 | 3.4 | 3.9 |
| Val di Fassa Sorda 4 | AE | 5-15 | 7.5YR 2.5/1 | 22 | 0.61 | 660 | 210 | 130 | 3.7 | 182.7 | 9.10 | 135.76 | 10.7 | 13.9 |
| | Bs1 | 15-32 | 5YR 3/2 | 57 | 0.46 | 530 | 380 | 88 | 4.4 | 85.8 | 3.80 | 85.33 | 26.7 | 18.2 |
| | Bs2 | 32-50 | 7.5YR 3/3 | 40 | 0.92 | 590 | 360 | 50 | 4.8 | 71.3 | 3.00 | 15.48 | 27.7 | 14.8 |
| | BC1 | 50-90 | 7.5YR 4/4 | 84 | 1.54 | 620 | 260 | 120 | 4.9 | 31.3 | 1.60 | 12.29 | 15.8 | 5.9 |
| | BC2 | 90-130 | 7.5YR 3/4 | 83 | 1.52 | 850 | 108 | 42 | 4.9 | 8.1 | 0.40 | 4.75 | 6.0 | 4.4 |
| | C | >130 | 10YR 3/4 | 73 | 1.51 | 820 | 139 | 41 | 5.0 | 2.3 | 0.30 | 4.91 | 4.7 | 4.4 |
| S. Nicolò 2 | E | 17-28 | 7.5YR 3/3 | 65 | 0.35 | 480 | 220 | 300 | 4.0 | 144.2 | 7.20 | 161.99 | 18.2 | 15.5 |
| | Bhs | 28-55 | 2.5YR 2.5/1 | 53 | 0.67 | 720 | 150 | 130 | 4.6 | 97.1 | 4.30 | 33.81 | 39.6 | 21.4 |
| | Bs | 55-90 | 2.5YR 3/2 | 68 | 1.12 | 890 | 80 | 30 | 4.7 | 36.6 | 2.40 | 12.69 | 37.3 | 10.4 |
| | BC | 90-125 | 5YR 3/3 | 78 | 1.51 | 810 | 104 | 86 | 4.7 | 22.1 | 1.20 | 11.38 | 29.9 | 7.9 |
| | C | >125 | 7.5YR 3/3 | 40 | 1.50 | n.m. | n.m. | n.m. | n.m. | n.m. | n.m. | 7.48 | n.m. | n.m. |

[1]Size fractions: sand = 2000 - 50 µm, silt = 50 - 2 µm, clay < 2 µm
[2]Water-soluble phenolic materials
n.m. = not measured
n.d. = not detectable

**Table 3**
**Click here to download Table: Table3.doc**

Table 3

Geochemical characteristics and total content of heavy metals (total analysis of the bulk material including soil skeleton (> 2mm up to 200mm) and fine earth (< 2mm)) of the investigated soils

| Site and soil horizon | depth cm | $Al_2O_3$ % | $SiO_2$ % | $TiO_2$ % | CaO % | MgO % | $K_2O$ % | $Na_2O$ % | $Fe_2O_3$ % | $MnO_2$ % | Cd mg/kg | Cr mg/kg | Zn mg/kg | Cu mg/kg | Ni mg/kg | Pb mg/kg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| South-facing Val di Rabbi | | | | | | | | | | | | | | | | |
| *S6* | | | | | | | | | | | | | | | | |
| AE | 3-10 | 14.74 | 61.63 | 0.52 | 1.63 | 1.15 | 2.18 | 1.7 | 4.89 | 0.06 | <0.40 | 43.02 | 79.20 | 13.11 | 22.69 | 34.93 |
| Bs1 | 10-50 | 14.72 | 64.07 | 0.51 | 1.72 | 1.17 | 2.54 | 1.77 | 4.18 | 0.06 | <0.40 | 43.88 | 74.09 | 16.42 | 24.34 | 29.38 |
| Bs2 | 50-90 | 15.61 | 68.18 | 0.48 | 2.03 | 1.20 | 2.75 | 2.19 | 4.24 | 0.06 | 0.40 | 34.94 | 74.28 | 13.86 | 20.02 | 23.71 |
| BC | 90-125 | 15.57 | 67.8 | 0.70 | 2.25 | 1.62 | 2.84 | 2.15 | 5.03 | 0.07 | <0.40 | 37.36 | 76.09 | 18.75 | 20.51 | 23.43 |
| *S7* | | | | | | | | | | | | | | | | |
| AE | 0-10 | 12.38 | 56.86 | 0.35 | 1.74 | 1.10 | 2.43 | 1.27 | 3.97 | 0.06 | <0.40 | 71.03 | 69.68 | 8.40 | 89.36 | 36.32 |
| Bs1 | 30-45 | 15.37 | 67.71 | 0.38 | 2.64 | 1.47 | 2.75 | 2.38 | 3.96 | 0.05 | <0.40 | 85.58 | 71.83 | 12.48 | 65.36 | 23.42 |
| Bs2 | 45-70 | 15.15 | 67.37 | 0.38 | 3.08 | 2.59 | 2.48 | 2.41 | 4.44 | 0.06 | <0.40 | 174.60 | 63.91 | 15.22 | 102.88 | 21.71 |
| BC | 95-110 | 14.18 | 69.83 | 0.36 | 2.67 | 3.35 | 2.67 | 2.37 | 3.94 | 0.06 | n.m. | n.m. | n.m. | n.m. | n.m. | n.m. |
| C | 95-115 | 17.43 | 62.31 | 0.53 | 0.72 | 1.60 | 2.58 | 2.22 | 5.86 | 0.07 | <0.40 | 179.61 | 72.50 | 23.40 | 180.10 | 18.40 |
| Val di Fassa | | | | | | | | | | | | | | | | |
| *Sorda 1* | | | | | | | | | | | | | | | | |
| A | 2-10 | 17.06 | 44.51 | 1.03 | 4.74 | 5.86 | 1.76 | 1.62 | 9.52 | 0.19 | <0.40 | 130.61 | 79.45 | 60.28 | 46.91 | 27.89 |
| BA | 20-37 | 17.47 | 46.6 | 1.06 | 5.2 | 6.59 | 1.79 | 1.62 | 9.85 | 0.16 | <0.40 | 145.29 | 79.73 | 65.46 | 51.27 | 14.19 |
| Bs | 37-55 | 17.18 | 47.74 | 1.00 | 5.34 | 7.17 | 1.65 | 1.55 | 9.29 | 0.18 | <0.40 | 130.31 | 80.00 | 75.84 | 45.95 | 13.68 |
| CB | 55-80 | 16.76 | 47.98 | 0.98 | 5.89 | 7.12 | 1.96 | 1.72 | 9.53 | 0.17 | <0.40 | 145.17 | 81.48 | 79.03 | 48.78 | 9.48 |
| *San Nicolò 4* | | | | | | | | | | | | | | | | |
| AE | 4-12 | 14.53 | 38.04 | 0.97 | 6.27 | 5.40 | 1.43 | 1.53 | 11.53 | 0.2 | <0.40 | 176.96 | 100.76 | 77.59 | 45.12 | 23.09 |
| BA | 12-28 | 15.29 | 39.82 | 1.02 | 6.16 | 5.34 | 1.51 | 1.33 | 11.82 | 0.21 | <0.40 | 177.37 | 102.93 | 78.02 | 46.14 | 23.14 |
| Bs1 | 28-50 | 16.58 | 42.13 | 1.11 | 6.02 | 5.09 | 1.69 | 1.32 | 11.86 | 0.18 | <0.40 | 160.65 | 99.60 | 79.87 | 49.16 | 20.07 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Bs2 | 50-82 | 17.48 | 41.04 | 1.12 | 4.74 | 5.01 | 1.71 | 0.92 | 11.84 | 0.16 | <0.40 | 146.80 | 96.22 | 68.40 | 48.35 | 16.18 |
| BC1 | 82-120 | 17.95 | 43.80 | 1.11 | 5.07 | 5.15 | 1.78 | 0.95 | 11.62 | 0.17 | <0.40 | 144.88 | 92.38 | 80.00 | 50.87 | 17.00 |
| BC2 | >150 | 17.23 | 46.30 | 1.10 | 6.39 | 5.49 | 2.05 | 1.34 | 11.77 | 0.18 | <0.40 | 144.13 | 86.93 | 85.91 | 50.57 | 15.52 |
| North-facing | | | | | | | | | | | | | | | | |
| Val di Rabbi | | | | | | | | | | | | | | | | |
| *N2* | | | | | | | | | | | | | | | | |
| E | 6-12 | 11.55 | 65.26 | 0.92 | 1.01 | 1.33 | 1.73 | 1.08 | 4.47 | 0.12 | <0.40 | 159.19 | 54.98 | 17.46 | 41.44 | 23.89 |
| Bs1 | 12-50 | 15.69 | 62.36 | 0.77 | 1.27 | 1.7 | 2.29 | 1.70 | 6.20 | 0.20 | <0.40 | 118.76 | 72.90 | 35.27 | 58.54 | 18.10 |
| Bs2 | 50-100 | 15.78 | 62.09 | 0.78 | 1.86 | 2.34 | 2.26 | 1.89 | 6.60 | 0.62 | <0.40 | 152.41 | 83.00 | 49.03 | 104.17 | 17.81 |
| C | 130-150 | 15.57 | 67.65 | 0.63 | 1.45 | 1.99 | 2.34 | 2.32 | 5.13 | 0.20 | <0.40 | 86.43 | 94.23 | 33.55 | 60.44 | 16.24 |
| *N3* | | | | | | | | | | | | | | | | |
| EA | 1-10 | 11.51 | 37.49 | 0.59 | 0.59 | 0.58 | 1.65 | 0.92 | 3.56 | 0.04 | <0.40 | 54.30 | 48.60 | 20.70 | 15.00 | 44.10 |
| Bhs | 10-25 | 15.69 | 53.05 | 0.78 | 1.16 | 1.87 | 2.30 | 1.34 | 7.00 | 0.08 | <0.40 | 99.49 | 77.75 | 18.06 | 17.37 | 27.28 |
| Bs | 25-57 | 17.00 | 57.75 | 0.72 | 1.41 | 2.27 | 2.88 | 1.34 | 6.61 | 0.08 | 1.37 | 101.05 | 98.17 | 27.38 | 20.68 | 23.21 |
| C | 80-110 | 18.02 | 60.48 | 0.75 | 1.38 | 2.57 | 3.05 | 1.85 | 6.33 | 0.08 | <0.40 | 104.03 | 102.27 | 39.51 | 25.79 | 20.49 |
| Val di Fassa | | | | | | | | | | | | | | | | |
| *Sorda 4* | | | | | | | | | | | | | | | | |
| AE | 5-15 | 12.68 | 32.79 | 0.97 | 2.25 | 2.41 | 1.25 | 1.07 | 8.00 | 0.09 | <0.40 | 52.65 | 60.17 | 45.58 | 30.63 | 110.74 |
| Bs1 | 15-32 | 16.93 | 35.62 | 1.08 | 4.10 | 4.26 | 1.36 | 1.63 | 10.01 | 0.15 | <0.40 | 85.37 | 74.96 | 118.81 | 45.68 | 29.30 |
| Bs2 | 32-50 | 19.54 | 38.98 | 1.2 | 3.69 | 4.11 | 1.44 | 1.47 | 10.88 | 0.16 | <0.40 | 85.60 | 83.52 | 68.87 | 49.35 | 17.00 |
| BC1 | 50-90 | 18.62 | 44.46 | 1.18 | 7.38 | 5.79 | 1.83 | 1.8 | 11.03 | 0.19 | <0.40 | 90.25 | 85.62 | 105.71 | 54.78 | 18.22 |
| BC2 | 90-130 | 18.1 | 45.52 | 1.17 | 7.92 | 6.31 | 1.70 | 1.89 | 10.83 | 0.21 | <0.40 | 95.51 | 83.36 | 92.33 | 53.18 | 15.00 |
| C | >140 | 17.91 | 45.82 | 1.18 | 8.09 | 5.73 | 1.86 | 1.86 | 10.8 | 0.19 | <0.40 | 91.72 | 84.08 | 97.46 | 50.44 | 11.63 |
| *San Nicolò 2* | | | | | | | | | | | | | | | | |
| E | 17-28 | 15.58 | 41.26 | 1.15 | 4.34 | 5.53 | 1.39 | 2.44 | 9.73 | 0.17 | <0.40 | 64.39 | 92.24 | 41.64 | 31.15 | 35.32 |
| Bhs | 28-55 | 17.18 | 33.65 | 1.19 | 4.04 | 5.79 | 1.26 | 2.01 | 11.58 | 0.14 | <0.40 | 67.23 | 82.13 | 44.34 | 36.11 | 12.36 |
| Bs | 55-90 | 19.48 | 39.10 | 1.13 | 4.68 | 6.31 | 1.46 | 2.38 | 10.58 | 0.16 | <0.40 | 62.82 | 79.25 | 52.08 | 38.00 | 14.65 |
| BC | 90-125 | 17.62 | 43.51 | 1.15 | 5.28 | 7.56 | 1.44 | 2.89 | 10.49 | 0.18 | <0.40 | 60.63 | 88.49 | 51.32 | 35.54 | 15.56 |
| C | >125 | 18.32 | 42.69 | 1.11 | 5.26 | 7.44 | 1.43 | 2.28 | 10.94 | 0.17 | <0.40 | 70.56 | 83.42 | 65.20 | 54.65 | 14.59 |

n.m. not measured

**Table 4**
**Click here to download Table: Table4.doc**

Table 4

Heavy metals speciation of the fine earth: total content (derived from XRF-analyses), weakly bound fraction (EDTA-extractable fraction) and the strongly-bound fraction (total content – EDTA fraction). All units are in mg/kg, except fort he weakly-bound fraction of Cd and Cr (µg/kg).

| Site / soil horizon | depth | Total content | | | | | | Strongly-bound[1)] | | | | | | Weakly-bound[2)] | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | cm | Cd mg/kg | Cr mg/kg | Zn mg/kg | Cu mg/kg | Ni mg/kg | Pb mg/kg | Cd mg/kg | Cr mg/kg | Zn mg/kg | Cu mg/kg | Ni mg/kg | Pb mg/kg | Cd µg/kg | Cr µg/kg | Zn mg/kg | Cu mg/kg | Ni mg/kg | Pb mg/kg |
| South-facing | | | | | | | | | | | | | | | | | | | |
| Val di Rabbi | | | | | | | | | | | | | | | | | | | |
| *S6* | | | | | | | | | | | | | | | | | | | |
| AE | 3-10 | <0.40 | 40.7 | 79.1 | 12.5 | 23.2 | 37.2 | nd[3)] | 40.5 | 78.8 | 12.0 | 23.1 | 34.4 | 22.2 | 185.8 | 0.274 | 0.526 | 0.135 | 2.793 |
| Bs1 | 10-50 | <0.40 | 49.9 | 79.2 | 18.7 | 27.6 | 31.0 | nd | 49.7 | 79.1 | 18.1 | 27.5 | 29.1 | 18.7 | 150.8 | 0.12 | 0.592 | 0.096 | 1.882 |
| Bs2 | 50-90 | 0.40 | 45.3 | 82.1 | 17.6 | 25.7 | 25.4 | 0.39 | 45.2 | 82.1 | 17.3 | 25.7 | 24.7 | 10.9 | 75.2 | 0.01 | 0.295 | 0.027 | 0.697 |
| BC | 90-125 | <0.40 | 45.4 | 86.0 | 28.8 | 25.5 | 24.4 | nd | 45.4 | 86.0 | 28.6 | 25.5 | 23.8 | 8.4 | 47.8 | 0.024 | 0.233 | 0.018 | 0.581 |
| *S7* | | | | | | | | | | | | | | | | | | | |
| AE | 0-10 | <0.40 | 70.0 | 77.6 | 10.2 | 36.6 | 44.2 | nd | 69.5 | 75.7 | 9.3 | 35.4 | 36.4 | 96.7 | 532.0 | 1.944 | 0.882 | 1.178 | 7.824 |
| BA | 10-30 | <0.40 | 92.0 | 78.0 | 12.0 | 50.0 | 32.0 | nd | 91.6 | 78.0 | 11.9 | 49.6 | 30.7 | 23.9 | 416.0 | 0.033 | 0.136 | 0.410 | 1.303 |
| Bs1 | 30-45 | <0.40 | 112.9 | 81.0 | 13.3 | 77.9 | 22.7 | nd | 112.7 | 80.9 | 13.3 | 77.8 | 22.5 | 7.5 | 153.3 | 0.09 | 0.045 | 0.101 | 0.246 |
| Bs2 | 45-70 | <0.40 | 212.0 | 71.9 | 15.8 | 123.2 | 22.0 | nd | 211.9 | 71.8 | 15.8 | 123.1 | 21.8 | 8.4 | 91.4 | 0.076 | 0.036 | 0.070 | 0.163 |
| BC | 70-95 | <0.40 | 263.6 | 72.5 | 23.4 | 180.1 | 18.4 | nd | 263.5 | 72.5 | 23.4 | 180.0 | 18.2 | 8.2 | 76.8 | < 0.01 | 0.030 | 0.060 | 0.156 |
| C | 95-110 | <0.40 | 242.6 | 71.2 | 14.8 | 206.6 | 20.5 | nd | 242.5 | 71.0 | 14.8 | 206.5 | 20.4 | <0.5 | 60.0 | 0.233 | 0.025 | 0.062 | 0.126 |
| Val di Fassa | | | | | | | | | | | | | | | | | | | |
| *Sorda 1* | | | | | | | | | | | | | | | | | | | |
| A | 2-10 | <0.40 | 122.0 | 80.0 | 57.0 | 48.0 | 35.0 | nd | 121.9 | 79.5 | 54.5 | 47.8 | 26.5 | 75.7 | 128.3 | 0.496 | 2.465 | 0.175 | 8.484 |
| BA | 20-37 | <0.40 | 142.0 | 81.0 | 68.0 | 50.0 | 18.0 | nd | 141.9 | 81.0 | 65.4 | 50.0 | 14.5 | 35.1 | 104.5 | < 0.01 | 2.568 | 0.045 | 3.510 |
| Bs | 37-55 | <0.40 | 127.0 | 80.0 | 75.0 | 51.0 | 12.0 | nd | 126.9 | 80.0 | 73.1 | 51.0 | 11.3 | 25.2 | 75.9 | < 0.01 | 1.950 | 0.015 | 0.733 |
| CB | 55-80 | <0.40 | 140.0 | 80.0 | 82.0 | 51.0 | 8.0 | nd | 139.9 | 79.6 | 80.3 | 51.0 | 7.8 | 16.8 | 75.0 | 0.378 | 1.722 | 0.021 | 0.216 |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *San Nicolò 4* | | | | | | | | | | | | | | | | | | |
| AE | 4-12 | <0.40 | 182.0 | 99.0 | 71.0 | 46.0 | 31.0 | nd | 181.8 | 98.6 | 67.2 | 45.8 | 26.4 | 27.5 | 168.3 | 0.369 | 3.844 | 0.238 | 4.601 |
| BA | 12-28 | <0.40 | 170.0 | 101.0 | 73.0 | 50.0 | 27.0 | nd | 169.8 | 100.9 | 68.6 | 49.8 | 22.2 | 26.7 | 161.3 | 0.053 | 4.396 | 0.197 | 4.841 |
| Bs1 | 28-50 | <0.40 | 156.0 | 95.0 | 69.0 | 50.0 | 23.0 | nd | 155.9 | 95.0 | 64.7 | 49.9 | 20.9 | 18.0 | 117.3 | < 0.01 | 4.326 | 0.125 | 2.112 |
| Bs2 | 50-82 | <0.40 | 141.0 | 91.0 | 64.0 | 50.0 | 17.0 | nd | 140.9 | 91.0 | 61.0 | 49.9 | 16.0 | 11.1 | 138.8 | 0.032 | 2.978 | 0.065 | 1.010 |
| BC1 | 82-120 | <0.40 | 148.0 | 89.0 | 74.0 | 52.0 | 14.0 | nd | 147.8 | 89.0 | 69.3 | 52.0 | 13.2 | 4.6 | 162.3 | 0.046 | 4.744 | 0.025 | 0.800 |
| BC2 | >150 | <0.40 | 132.0 | 80.0 | 77.0 | 57.0 | 17.0 | nd | 131.9 | 80.0 | 73.6 | 57.0 | 16.5 | 2.4 | 131.8 | < 0.01 | 3.428 | 0.001 | 0.499 |
| North-facing | | | | | | | | | | | | | | | | | | | |
| Val di Rabbi | | | | | | | | | | | | | | | | | | | |
| *N2* | | | | | | | | | | | | | | | | | | | |
| E | 6-12 | <0.40 | 112.7 | 50.1 | 20.6 | 39.4 | 33.9 | nd | 111.4 | 48.7 | 20.1 | 38.7 | 22.8 | 15.3 | 1280.0 | 1.408 | 0.483 | 0.661 | 11.140 |
| Bs1 | 12-50 | <0.40 | 164.1 | 79.3 | 41.0 | 74.9 | 21.6 | nd | 163.5 | 79.1 | 40.5 | 74.6 | 20.1 | 48.1 | 596.0 | 0.158 | 0.480 | 0.341 | 1.541 |
| Bs2 | 50-100 | <0.40 | 224.3 | 108.2 | 55.8 | 129.3 | 18.7 | nd | 223.9 | 108.1 | 55.4 | 129.2 | 17.8 | 27.7 | 384.0 | 0.081 | 0.431 | 0.076 | 0.935 |
| BC | 100-130 | <0.40 | 170.0 | 100.0 | 45.0 | 95.0 | 21.0 | nd | 169.8 | 99.9 | 44.7 | 94.9 | 20.3 | 15.5 | 188.0 | 0.055 | 0.290 | 0.051 | 0.688 |
| C | 130-150 | <0.40 | 114.9 | 93.4 | 39.0 | 66.8 | 22.6 | nd | 114.8 | 93.4 | 38.9 | 66.8 | 22.0 | 2.3 | 89.2 | < 0.01 | 0.109 | 0.044 | 0.579 |
| *N3* | | | | | | | | | | | | | | | | | | | |
| EA | 1-10 | <0.40 | 54.3 | 48.6 | 20.7 | 15.0 | 44.1 | nd | 53.8 | 48.0 | 20.2 | 14.6 | 39.7 | 12.8 | 454.0 | 0.564 | 0.461 | 0.407 | 4.439 |
| E | 10-12 | <0.40 | 87.0 | 63.0 | 20.0 | 16.0 | 37.0 | nd | 86.5 | 62.3 | 18.6 | 14.8 | 31.2 | 9.5 | 466.0 | 0.701 | 1.376 | 1.185 | 5.762 |
| Bhs | 12-25 | <0.40 | 102.5 | 73.9 | 18.5 | 16.0 | 29.5 | nd | 101.2 | 73.8 | 17.8 | 15.8 | 28.5 | 6.2 | 1336.0 | 0.055 | 0.675 | 0.244 | 0.991 |
| Bs | 25-57 | 2.10 | 115.1 | 103.7 | 34.3 | 21.8 | 24.2 | 2.09 | 114.6 | 103.6 | 33.7 | 21.7 | 24.1 | 8.0 | 546.0 | 0.063 | 0.585 | 0.109 | 0.057 |
| BC | 57-80 | <0.40 | 125.0 | 115.0 | 44.0 | 25.0 | 23.0 | nd | 124.8 | 114.8 | 43.7 | 24.9 | 23.0 | 2.7 | 246.0 | 0.227 | 0.339 | 0.075 | 0.017 |
| C | 80-110 | <0.40 | 130.8 | 118.8 | 51.7 | 27.3 | 22.5 | nd | 130.7 | 118.5 | 51.5 | 27.3 | 22.5 | 1.2 | 84.1 | 0.261 | 0.225 | 0.031 | 0.036 |
| Val di Fassa | | | | | | | | | | | | | | | | | | | |
| *Sorda 4* | | | | | | | | | | | | | | | | | | | |
| AE | 5-15 | <0.40 | 62.0 | 52.0 | 33.0 | 26.0 | 122.0 | nd | 61.4 | 51.0 | 29.6 | 24.6 | 75.2 | 93.1 | 586.0 | 0.966 | 3.382 | 1.443 | 46.800 |
| Bs1 | 15-32 | <0.40 | 103.0 | 59.0 | 43.0 | 32.0 | 35.0 | nd | 102.6 | 58.6 | 39.1 | 31.0 | 26.1 | 171.2 | 384.0 | 0.401 | 3.914 | 1.047 | 8.896 |
| Bs2 | 32-50 | <0.40 | 85.0 | 76.0 | 57.0 | 45.0 | 17.0 | nd | 84.8 | 76.0 | 55.8 | 44.9 | 16.3 | 22.4 | 212.3 | < 0.01 | 1.216 | 0.051 | 0.681 |
| BC1 | 50-90 | <0.40 | 89.0 | 89.0 | 115.0 | 59.0 | 14.0 | nd | 88.9 | 89.0 | 114.5 | 59.0 | 13.8 | 12.5 | 88.8 | < 0.01 | 0.535 | 0.023 | 0.154 |
| BC2 | 90-130 | <0.40 | 95.0 | 95.0 | 89.0 | 59.0 | 15.0 | nd | 95.0 | 94.6 | 88.7 | 59.0 | 14.8 | 5.2 | 49.2 | 0.434 | 0.283 | 0.009 | 0.162 |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | >140 | <0.40 | 89.0 | 95.0 | 96.0 | 65.0 | 16.0 | nd | 89.0 | 95.0 | 95.7 | 65.0 | 15.8 | 5.3 | 46.9 | < 0.01 | 0.329 | 0.001 | 0.161 |
| *San Nicolò 2* | | | | | | | | | | | | | | | | | | | |
| E | 17-28 | <0.40 | 70.0 | 76.0 | 28.0 | 24.0 | 60.0 | nd | 69.4 | 75.5 | 26.1 | 23.5 | 48.2 | 1.2 | 554.0 | 0.489 | 1.926 | 0.475 | 11.840 |
| Bhs | 28-55 | <0.40 | 71.0 | 61.0 | 38.0 | 34.0 | 15.0 | nd | 70.7 | 60.8 | 36.1 | 33.5 | 12.2 | 14.0 | 266.3 | 0.243 | 1.876 | 0.545 | 2.792 |
| Bs | 55-90 | <0.40 | 68.0 | 61.0 | 46.0 | 38.0 | 16.0 | nd | 67.9 | 60.4 | 45.3 | 37.9 | 15.9 | 2.7 | 64.8 | 0.632 | 0.748 | 0.149 | 0.138 |
| BC | 90-125 | <0.40 | 58.0 | 76.0 | 56.0 | 41.0 | 14.0 | nd | 58.0 | 76.0 | 55.5 | 41.0 | 13.9 | 1.6 | 34.2 | < 0.01 | 0.480 | 0.013 | 0.092 |
| C | >125 | <0.40 | 60.0 | 79.0 | 66.0 | 45.0 | 17.0 | nd | 60.0 | 79.0 | 65.5 | 45.0 | 16.9 | 2.0 | 35.0 | < 0.01 | 0.483 | 0.002 | 0.116 |

[1)] stronger bound fraction (including specifically-bound species, co-precipitations, amorphous or crystalline phases) = Total content – EDTA-extractable content.
[2)] weakly bound species (organically bound species, species bound to oxyhydroxides, adsorbed species, easily soluble species) corresponds to the EDTA-extractable fraction
[3)] nd = not determined

Table 5.
Multiple regression model with the heavy metals (EDTA-extractable) as dependent variables and pH, org. C, $Fe_o$ and clay content as independent variables. The multiple linear regression has the form: log [heavy metal] = intercept + $a_1$pH + $a_2$ [log (org. C)] + $a_3$ [log($Fe_o$)] + $a_4$ [log(Clay)].

| Element/ variable | Regression coefficient (a) | Error probability (p) | $R^2$ |
|---|---|---|---|
| log(Cd) | | | 0.26 |
| intercept | -0.935 | | |
| pH | 0.203 | 0.311 | |
| log [org. C (g/kg)] | 0.558 | 0.155 | |
| log [$Fe_o$ (g/kg)] | 0.259 | 0.552 | |
| log [Clay (g/kg)] | 0.006 | 0.988 | |
| log(Cr) | | | 0.80** |
| intercept | 4.026 | | |
| pH | -0.551 | <0.001 | |
| log [org. C (g/kg)] | -0.351 | 0.028 | |
| log [$Fe_o$ (g/kg)] | 0.713 | <0.001 | |
| log [Clay (g/kg)] | 0.339 | 0.043 | |
| log(Zn) | | | 0.27 |
| intercept | -1.423 | | |
| pH | -0.058 | 0.802 | |
| log [org. C (g/kg)] | 0.462 | 0.312 | |
| log [$Fe_o$ (g/kg)] | -0.543 | 0.277 | |
| log [Clay (g/kg)] | 0.408 | 0.423 | |
| log(Cu) | | | 0.75** |
| intercept | -4.38 | | |
| pH | 0.394 | 0.003 | |
| log [org. C (g/kg)] | 0.214 | 0.371 | |
| log [$Fe_o$ (g/kg)] | 0.924 | 0.002 | |
| log [Clay (g/kg)] | 0.656 | 0.013 | |
| log(Ni) | | | 0.71** |
| intercept | -0.616 | | |
| pH | -0.365 | 0.022 | |
| log [org. C (g/kg)] | 0.766 | 0.014 | |
| log [$Fe_o$ (g/kg)] | -0.148 | 0.659 | |
| log [Clay (g/kg)] | 0.175 | 0.576 | |
| Log(Pb) | | | 0.65** |
| intercept | -2.551 | | |
| pH | -0.071 | 0.710 | |
| log [org. C (g/kg)] | 0.614 | 0.106 | |

| | | |
|---|---|---|
| log [$Fe_o$ (g/kg)] | -0.288 | 0.497 |
| log [Clay (g/kg)] | 1.201 | 0.004 |

* error probability (multiple regression) < 0.05
** error probability (multiple regression) < 0.01

**Table 6**
**Click here to download Table: Table6.doc**

Table 6
Mass transport functions (τ) for each element investigated with respect to the sites and soil depth and mass losses (negative values, g/m$^2$) and gains (positive values, g/m$^2$) for heavy metals.

| Site/ horizons | depth cm | Al (τ) | Si (τ) | Ca (τ) | Mg (τ) | K (τ) | Na (τ) | Fe (τ) | Mn (τ) | Cr (τ) | Zn (τ) | Cu (τ) | Ni (τ) | Pb (τ) | Cr (g/m$^2$) | Zn (g/m$^2$) | Cu (g/m$^2$) | Ni (g/m$^2$) | Pb (g/m$^2$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| South-facing | | | | | | | | | | | | | | | | | | | |
| *Val di Rabbi* | | | | | | | | | | | | | | | | | | | |
| *S6* | | | | | | | | | | | | | | | | | | | |
| AE | 3-10 | -0.12 | -0.16 | -0.33 | -0.35 | -0.29 | -0.27 | -0.10 | -0.20 | 0.07 | -0.04 | -0.35 | 0.02 | 0.38 | 0.39 | -0.46 | -1.06 | 0.08 | 1.41 |
| Bs1 | 10-50 | -0.11 | -0.11 | -0.28 | -0.32 | -0.16 | -0.22 | -0.22 | -0.23 | 0.11 | -0.08 | -0.17 | 0.12 | 0.18 | 1.30 | -2.01 | -1.06 | 0.79 | 1.39 |
| Bs2 | 50-90 | 0.00 | 0.01 | -0.10 | -0.27 | -0.03 | 0.02 | -0.16 | -0.13 | -0.07 | -0.02 | -0.26 | -0.02 | 0.01 | -1.10 | -0.82 | -2.21 | -0.22 | 0.13 |
| BC | 90-125 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| *S7* | | | | | | | | | | | | | | | | | | | |
| AE | 0-10 | -0.10 | -0.16 | -0.33 | -0.66 | -0.07 | -0.45 | 0.03 | -0.01 | -0.59 | -0.01 | -0.63 | -0.49 | 1.03 | -21.83 | -0.20 | -3.02 | -18.08 | 3.86 |
| Bs1 | 30-45 | 0.03 | -0.08 | -0.06 | -0.58 | -0.02 | -0.04 | -0.05 | -0.21 | -0.55 | -0.06 | -0.49 | -0.66 | 0.21 | -22.00 | -0.94 | -2.58 | -26.41 | 0.87 |
| Bs2 | 45-70 | 0.02 | -0.08 | 0.10 | -0.26 | -0.11 | -0.03 | 0.08 | -0.02 | -0.07 | -0.16 | -0.38 | -0.46 | 0.13 | -10.96 | -9.71 | -7.49 | -69.11 | 1.95 |
| C | 95-110 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| *Val di Fassa* | | | | | | | | | | | | | | | | | | | |
| Sorda 1 | | | | | | | | | | | | | | | | | | | |
| A | 0-20 | -0.03 | -0.11 | -0.23 | -0.21 | -0.15 | -0.10 | -0.05 | 0.01 | -0.14 | -0.07 | -0.27 | -0.08 | 1.81 | -3.73 | -1.03 | -3.91 | -0.73 | 3.11 |
| BA | 20-37 | -0.03 | -0.10 | -0.18 | -0.14 | -0.15 | -0.12 | -0.04 | -0.14 | -0.07 | -0.09 | -0.23 | -0.02 | 0.39 | -1.83 | -1.34 | -3.33 | -0.19 | 0.68 |
| Bs | 37-55 | 0.01 | -0.02 | -0.11 | -0.01 | -0.17 | -0.11 | -0.04 | 0.01 | -0.12 | -0.03 | -0.05 | -0.07 | 0.42 | -3.60 | -0.57 | -0.92 | -0.75 | 0.86 |
| C | >55 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| S. Nicolò 4 | | | | | | | | | | | | | | | | | | | |
| AE | 4-12 | -0.04 | -0.06 | 0.12 | 0.12 | -0.21 | 0.30 | 0.12 | 0.24 | 0.40 | 0.32 | 0.03 | 0.02 | 0.70 | 4.68 | 2.27 | 0.20 | 0.07 | 0.88 |
| BA | 12-28 | -0.04 | -0.07 | 0.04 | 0.05 | -0.20 | 0.07 | 0.09 | 0.21 | 0.33 | 0.28 | -0.02 | -0.01 | 0.62 | 5.44 | 2.79 | -0.15 | -0.06 | 1.08 |
| Bs1 | 28-50 | -0.04 | -0.09 | -0.06 | -0.07 | -0.18 | -0.02 | 0.00 | -0.02 | 0.11 | 0.14 | -0.07 | -0.03 | 0.29 | 3.04 | 2.34 | -1.18 | -0.29 | 0.85 |
| Bs2 | 50-82 | 0.00 | -0.12 | -0.27 | -0.10 | -0.18 | -0.32 | -0.01 | -0.14 | 0.01 | 0.09 | -0.21 | -0.06 | 0.03 | 0.23 | 2.16 | -4.89 | -0.75 | 0.12 |
| BC1 | 82-120 | 0.00 | -0.06 | -0.21 | -0.06 | -0.14 | -0.30 | -0.02 | -0.11 | 0.00 | 0.06 | -0.07 | 0.00 | 0.09 | 0.22 | 3.17 | -3.73 | 0.10 | 0.88 |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BC2 | >125 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | | | | | |
| North-facing | | | | | | | | | | | | | | | | | | |
| *Val di Rabbi* | | | | | | | | | | | | | | | | | | |
| *N2* | | | | | | | | | | | | | | | | | | |
| E | 6-12 | -0.50 | -0.35 | -0.53 | -0.55 | -0.50 | -0.69 | -0.41 | -0.60 | 0.25 | -0.61 | -0.65 | -0.54 | 0.00 | 3.03 | -8.08 | -3.08 | -4.59 | -0.01 |
| Bs1 | 12-50 | -0.18 | -0.25 | -0.29 | -0.31 | -0.20 | -0.41 | -0.02 | -0.17 | 0.12 | -0.37 | -0.15 | -0.21 | -0.10 | 5.22 | -18.27 | -2.56 | -6.73 | -0.81 |
| Bs2 | 50-100 | -0.19 | -0.26 | 0.03 | -0.06 | -0.22 | -0.35 | 0.03 | 1.49 | 0.41 | -0.29 | 0.17 | 0.38 | -0.12 | 55.37 | -42.83 | 8.93 | 35.74 | -3.03 |
| C | 130-150 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | | | | | |
| *N3* | | | | | | | | | | | | | | | | | | |
| EA | 1-10 | -0.19 | -0.22 | -0.46 | -0.72 | -0.32 | -0.38 | -0.29 | -0.41 | -0.37 | -0.42 | -0.36 | -0.29 | 1.61 | -2.37 | -2.69 | -0.89 | -0.47 | 2.06 |
| Bhs | 12-25 | -0.16 | -0.16 | -0.19 | -0.30 | -0.28 | -0.31 | 0.06 | -0.06 | -0.12 | -0.30 | -0.58 | -0.38 | 0.23 | -2.65 | -6.68 | -5.02 | -2.14 | 1.04 |
| Bs | 25-57 | -0.02 | -0.01 | 0.06 | -0.08 | -0.02 | -0.25 | 0.09 | 0.05 | -0.03 | -0.04 | -0.31 | -0.20 | 0.13 | -1.85 | -2.55 | -7.54 | -3.18 | 1.69 |
| C | 80-110 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | | | | | |
| *Val di Fassa* | | | | | | | | | | | | | | | | | | |
| Sorda 4 | | | | | | | | | | | | | | | | | | |
| AE | 5-15 | -0.14 | -0.13 | -0.66 | -0.49 | -0.19 | -0.31 | -0.10 | -0.39 | -0.31 | -0.13 | -0.43 | -0.26 | 10.53 | -2.81 | -1.13 | -3.70 | -1.34 | 12.29 |
| Bs1 | 15-32 | -0.03 | -0.15 | -0.45 | -0.19 | -0.20 | -0.04 | 0.01 | -0.14 | 0.02 | -0.03 | 0.33 | -0.01 | 1.75 | 0.12 | -0.15 | 2.71 | -0.04 | 1.46 |
| Bs2 | 32-50 | 0.07 | -0.17 | -0.55 | -0.30 | -0.24 | -0.22 | -0.01 | -0.19 | -0.08 | -0.03 | -0.31 | -0.04 | 0.43 | -1.30 | -0.36 | -4.11 | -0.34 | 0.85 |
| BC1 | 50-90 | 0.04 | -0.03 | -0.09 | 0.01 | -0.02 | -0.03 | 0.01 | -0.01 | -0.02 | 0.02 | 0.09 | 0.09 | 0.57 | -0.88 | 0.97 | 8.45 | 2.68 | 4.05 |
| BC2 | 90-130 | 0.02 | 0.00 | -0.02 | 0.11 | -0.08 | 0.02 | 0.01 | 0.11 | 0.05 | 0.00 | -0.05 | 0.06 | 0.30 | 3.20 | -0.25 | 0.57 | 2.26 | 2.60 |
| C | >140 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | | | | | |
| S. Nicolò 2 | | | | | | | | | | | | | | | | | | |
| E | 17-28 | -0.18 | -0.07 | -0.20 | -0.28 | -0.06 | 0.04 | -0.14 | -0.05 | -0.12 | 0.07 | -0.38 | -0.45 | 1.34 | -0.93 | 0.58 | -2.54 | -2.50 | 1.99 |
| Bhs | 28-55 | -0.12 | -0.26 | -0.28 | -0.27 | -0.17 | -0.17 | -0.01 | -0.21 | -0.11 | -0.08 | -0.36 | -0.38 | -0.20 | -1.59 | -1.22 | -4.55 | -4.01 | -0.58 |
| Bs | 55-90 | 0.05 | -0.09 | -0.12 | -0.16 | 0.01 | 0.03 | -0.04 | -0.04 | -0.12 | -0.06 | -0.21 | -0.31 | -0.01 | -3.64 | -1.97 | -5.40 | -6.75 | -0.04 |
| BC | 90-125 | -0.06 | -0.01 | -0.02 | -0.01 | -0.02 | 0.24 | -0.07 | 0.05 | -0.16 | 0.03 | -0.23 | -0.37 | 0.04 | -6.73 | 1.42 | -8.31 | -10.91 | 0.30 |
| C | >125 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

**Table 7**
**Click here to download Table: Table7.doc**

Table 7
Amount (distribution) of total org. C and N and C/N ratios in the different density fractions

| Exposure/ valley, site | Horizon | Org. $C_{tot}$ (%) in | | | Sum | $N_{tot}$ (%) in | | | Sum | C/N | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | < 1g/cm$^3$ | 1-2g/cm$^3$ | > 2g/cm$^3$ | Tot. org C. % | < 1g/cm$^3$ | 1-2g/cm$^3$ | > 2g/cm$^3$ | Tot. N % | < 1g/cm$^3$ | 1-2g/cm$^3$ | > 2g/cm$^3$ |
| South-facing | | | | | | | | | | | | |
| Val di Rabbi | | | | | | | | | | | | |
| S6 | AE | 0.93 | 1.48 | 2.52 | 4.93 | 0.024 | 0.038 | 0.144 | 0.206 | 39.0 | 38.8 | 17.5 |
| | Bs1 | 0.34 | 1.97 | 1.50 | 3.81 | 0.006 | 0.053 | 0.092 | 0.151 | 56.6 | 37.2 | 16.3 |
| | Bs2 | 0.32 | 0.13 | 1.21 | 1.66 | 0.005 | 0.004 | 0.068 | 0.077 | 61.4 | 34.9 | 17.8 |
| S7 | AE | 1.10 | 3.16 | 4.33 | 8.59 | 0.052 | 0.183 | 0.298 | 0.534 | 21.0 | 17.2 | 14.5 |
| | BA | 0.13 | 3.01 | 3.31 | 6.45 | 0.002 | 0.144 | 0.196 | 0.342 | 51.4 | 21.0 | 16.9 |
| | Bs1 | 0.01 | 0.40 | 1.17 | 1.59 | 0.000 | 0.012 | 0.036 | 0.048 | 70.0 | 33.7 | 32.7 |
| Val di Fassa | | | | | | | | | | | | |
| Sorda 1 | A | 0.81 | 1.11 | 2.68 | 4.59 | 0.013 | 0.030 | 0.177 | 0.220 | 63.4 | 36.6 | 15.1 |
| | BA | 0.22 | 0.15 | 2.07 | 2.44 | 0.002 | 0.003 | 0.135 | 0.140 | 103.6 | 44.8 | 15.4 |
| | Bs | 0.12 | 0.82 | 1.16 | 2.09 | 0.003 | 0.031 | 0.116 | 0.150 | 42.8 | 26.2 | 10.0 |
| S. Nicolò 4 | AE | 1.06 | 3.56 | 3.11 | 7.73 | 0.037 | 0.203 | 0.260 | 0.500 | 29.1 | 17.5 | 11.9 |
| | BA | 0.47 | 1.15 | 3.43 | 5.06 | 0.012 | 0.060 | 0.298 | 0.370 | 38.9 | 19.3 | 11.5 |
| | Bs1 | 0.14 | 0.77 | 1.70 | 2.62 | 0.004 | 0.049 | 0.147 | 0.200 | 37.0 | 15.7 | 11.6 |
| North-facing | | | | | | | | | | | | |
| Val di Rabbi | | | | | | | | | | | | |
| N2 | E | 0.14 | 0.03 | 5.48 | 5.65 | 0.005 | 0.002 | 0.240 | 0.247 | 28.6 | 13.3 | 22.9 |
| | Bs1 | 1.04 | 0.05 | 1.22 | 2.31 | 0.037 | 0.002 | 0.044 | 0.083 | 28.0 | 25.0 | 27.8 |
| | Bs2 | 0.14 | 0.18 | 1.28 | 1.60 | 0.003 | 0.006 | 0.054 | 0.063 | 49.0 | 31.9 | 23.5 |
| N3 | EA | 5.61 | 10.96 | 2.85 | 19.42 | 0.304 | 0.637 | 0.176 | 1.117 | 18.5 | 17.2 | 16.2 |
| | E | 0.45 | 2.48 | 5.26 | 8.20 | 0.015 | 0.105 | 0.240 | 0.361 | 29.5 | 23.6 | 21.9 |
| | Bhs | 0.27 | 3.99 | 2.38 | 6.64 | 0.011 | 0.157 | 0.102 | 0.270 | 24.5 | 25.4 | 23.4 |
| Val di Fassa | | | | | | | | | | | | |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sorda 4 | AE | 0.74 | 0.40 | 17.13 | 18.27 | 0.029 | 0.021 | 0.859 | 0.910 | 25.2 | 19.0 | 19.9 |
| | Bs1 | 1.66 | 4.05 | 2.87 | 8.58 | 0.073 | 0.182 | 0.125 | 0.380 | 22.8 | 22.3 | 22.9 |
| | Bs2 | 0.14 | 3.87 | 3.12 | 7.13 | 0.005 | 0.159 | 0.136 | 0.300 | 28.0 | 24.4 | 22.9 |
| S. Nicolò 2 | E | 8.87 | 0.79 | 4.75 | 14.42 | 0.415 | 0.042 | 0.263 | 0.720 | 21.4 | 19.1 | 18.1 |
| | Bhs | 0.24 | 5.08 | 4.38 | 9.71 | 0.009 | 0.220 | 0.202 | 0.430 | 28.1 | 23.1 | 21.7 |
| | Bs | 0.12 | 2.10 | 1.44 | 3.66 | 0.006 | 0.140 | 0.094 | 0.240 | 19.6 | 15.0 | 15.4 |

**Table 8**
**Click here to download Table: Table8.doc**

Table 8
Carbon and nitrogen concentration in the soil before and after the $H_2O_2$ treatment. The recoveries give the ratio of the measured amount of C or N after the treatment to the initial amount

| Exposure/ valley, site | Horizon | Before the $H_2O_2$ treatment C g/kg | N g/kg | C/N | After the $H_2O_2$ treatment C g/kg | N g/kg | C/N | Recovery C % | N % | $^{14}C$ age [1] cal BP |
|---|---|---|---|---|---|---|---|---|---|---|
| South-facing | | | | | | | | | | |
| Val di Rabbi | | | | | | | | | | |
| S6 | AE | 49.3 | 2.06 | 23.9 | 6.2 | 0.32 | 19.4 | 11.4 | 14.1 | 8628 - 9007 |
| | Bs1 | 38.1 | 1.51 | 25.2 | 3.1 | 0.35 | 8.8 | 7.1 | 20.3 | 3443 - 3693 |
| | Bs2 | 16.6 | 0.77 | 21.6 | 10.1 | 0.49 | 20.7 | 59.3 | 61.8 | |
| S7 | AE | 85.9 | 5.34 | 16.1 | 17.1 | 0.85 | 20.1 | 16.8 | 13.4 | 16454 - 17453 |
| | BA | 64.5 | 3.42 | 18.9 | 5.8 | 0.46 | 12.5 | 7.8 | 11.7 | 4800 - 5042 |
| | Bs2 | 8.7 | 0.27 | 32.2 | 3.9 | 0.20 | 19.6 | 42.4 | 69.8 | 17185 - 18215 |
| Val di Fassa | | | | | | | | | | |
| S. Nicolò 4 | AE | 77.3 | 5.00 | 15.5 | 15.5 | 1.64 | 9.4 | 15.7 | 25.7 | 3584 - 3864 |
| | BA | 50.6 | 4.00 | 13.7 | 11.9 | 0.92 | 13.0 | 18.0 | 19.0 | 5590 - 5760 |
| | Bs2 | 20.3 | 2.00 | 13.6 | 7.9 | 0.80 | 9.9 | 30.9 | 42.6 | 7274 - 7504 |
| Sorda 1 | A | 45.9 | 2.00 | 20.9 | 8.0 | 0.29 | 27.6 | 13.8 | 10.5 | 3474 - 3731 |
| | BA | 24.4 | 1.00 | 17.4 | 6.0 | 0.19 | 31.7 | 21.2 | 11.7 | 6396 - 6660 |
| North-facing | | | | | | | | | | |
| Val di Rabbi | | | | | | | | | | |
| N2 | E | 56.5 | 2.47 | 22.9 | 10.6 | 1.03 | 10.3 | 10.5 | 23.3 | 11696 - 12248 |
| | Bs2 | 16.0 | 0.63 | 25.4 | 8.5 | 0.46 | 18.5 | 52.2 | 71.6 | 15834 - 16794 |
| N3 | EA | 194.2 | 11.17 | 17.4 | 10.6 | 3.72 | 2.9 | 3.8 | 23.3 | [2]14160 - 14964 |
| | E | 82.0 | 3.61 | 22.7 | 16.8 | 3.04 | 5.5 | 16.4 | 67.3 | [2]16782 - 17839 |
| | Bhs | 66.4 | 2.70 | 24.6 | 7.0 | 1.95 | 3.6 | 7.4 | 50.6 | [2]11274 - 11972 |
| | Bs | 28.0 | 1.01 | 27.7 | 3.5 | 1.01 | 3.5 | 10.0 | 80.0 | [2]10786 - 11270 |
| Val di Fassa | | | | | | | | | | |
| Sorda 4 | AE | 182.7 | 9.00 | 20.1 | 34.8 | 1.13 | 30.8 | 9.3 | 6.1 | 6276 - 6475 |
| | Bs1 | 85.8 | 4.00 | 22.6 | 13.6 | 0.63 | 21.5 | 9.7 | 10.2 | 5661 - 5930 |
| | Bs2 | 71.3 | 3.00 | 23.8 | 15.1 | 0.46 | 32.8 | 17.1 | 12.4 | 5920 - 6184 |
| S. Nicolò 2 | E | 144.2 | 7.00 | 20.0 | 26.6 | 0.73 | 36.4 | 14.9 | 8.2 | 4230 - 4522 |
| | Bhs | 97.1 | 4.00 | 22.6 | 12.8 | 0.32 | 40.0 | 8.1 | 4.6 | 2152 - 2370 |

[1] Radiocarbon data of the $H_2O_2$ resistant carbon fraction
[2] Radiocarbon data of a nearby soil (few meters)

**Figure captions**

Fig. 1. EDTA-extractable heavy metals abundance (of the whole soil profile) as a function of exposure.

Fig. 2. Mean organic matter stocks and corresponding density fractions (< 1 g/cm$^3$, 1–2 g/cm$^3$, > 2 g/cm$^3$) and abundance of labile ($H_2O_2$-oxidisable) and stable ($H_2O_2$-resitant) organic matter as a function of exposure.

Fig. 3. SEM micrographs with EDS analyses of the density fractions A) < 1 g/cm$^3$ B) 1-2 g/cm$^3$ and C) > 2 g/cm$^3$ of a surface soil sample.

Fig. 4. SEM micrographs with EDS analyses of an untreated and $H_2O_2$-treated soil sample of a Bs1 horizon.

Fig. 5. Relationship between the mass transport function $\tau$ of Al and Si (taken as weathering indicators) and the EDTA extractable content of Cr and Ni.

Fig. 6. Relationship between org. C and N in density fractions and heavy metals (Pb and Cu).

Fig. 7. Correlation between stable and labile organic C or N and the EDTA-extractable content of Cr, Ni and Pb.

Figure 1

Click here to download high resolution image

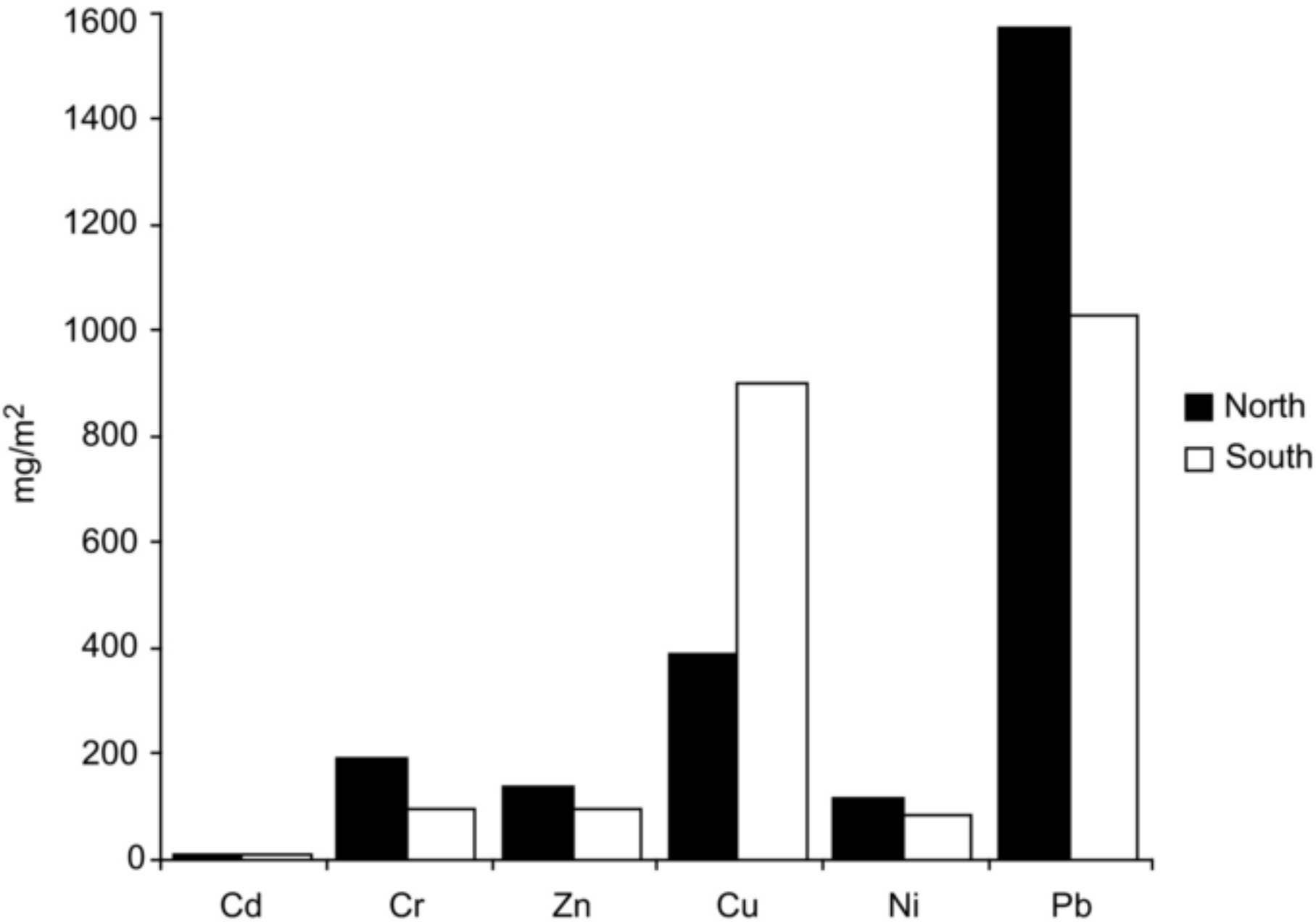

Figure 2

Click here to download high resolution image

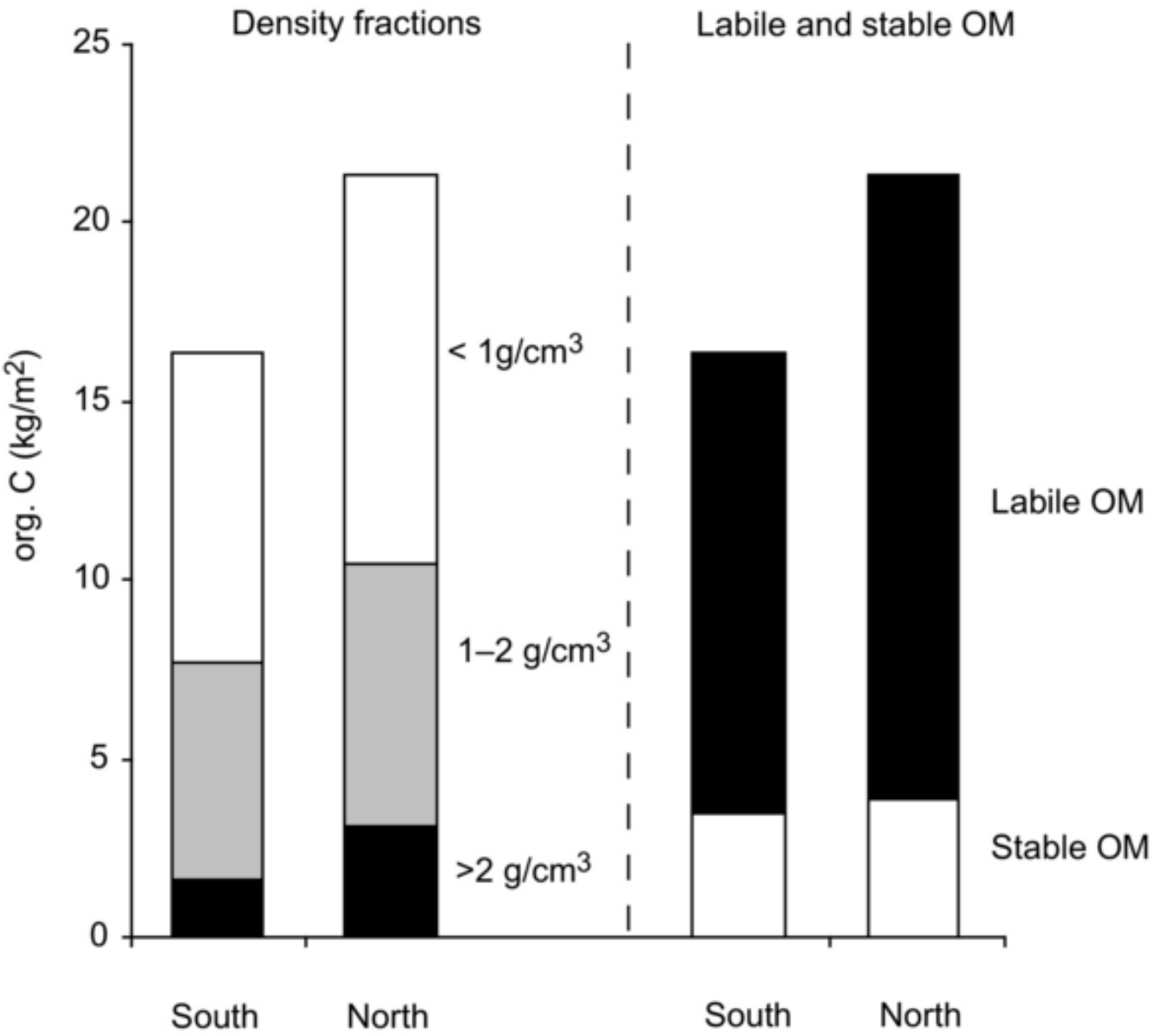

**Figure 3**

Click here to download high resolution image

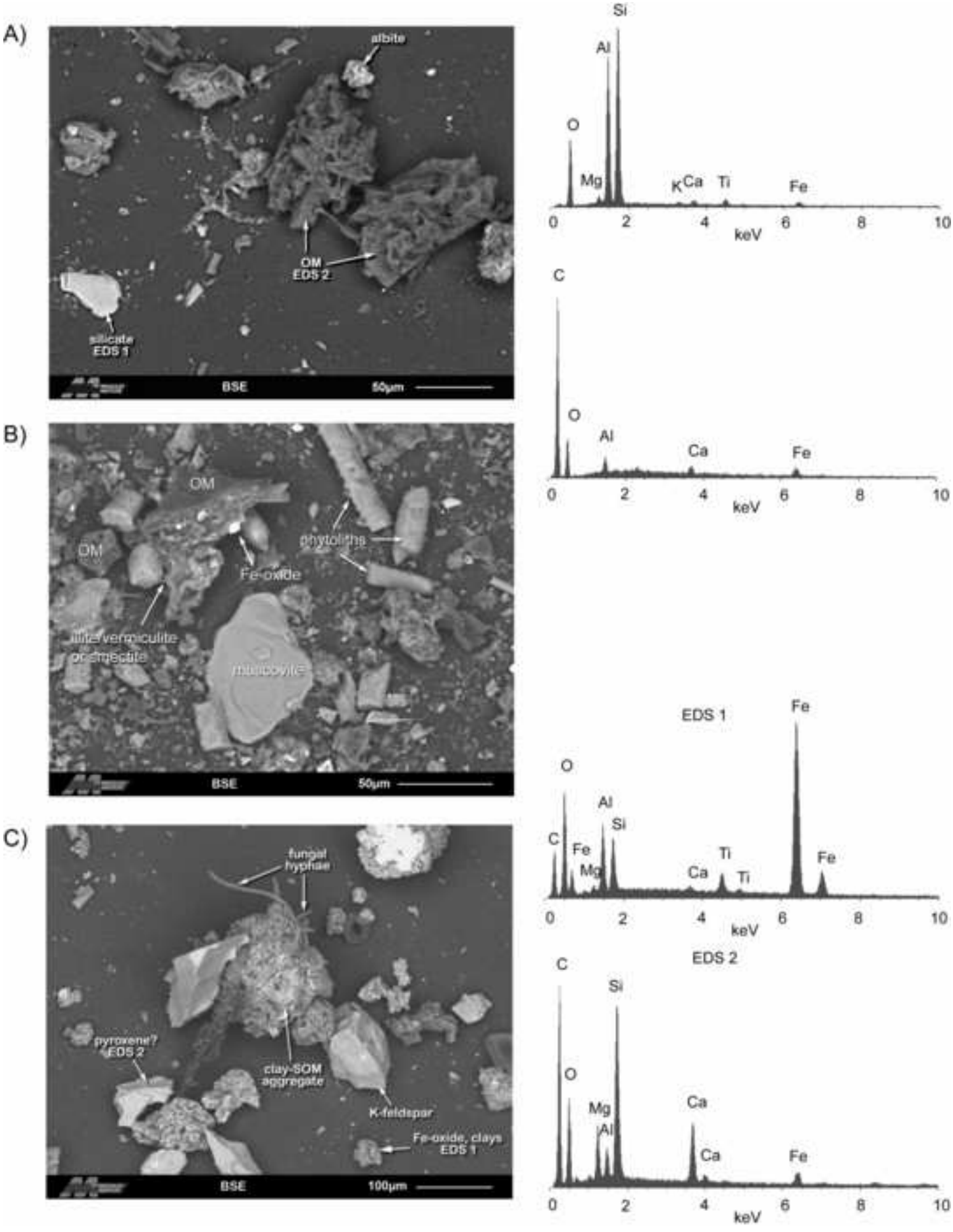

**Figure 4**

Click here to download high resolution image

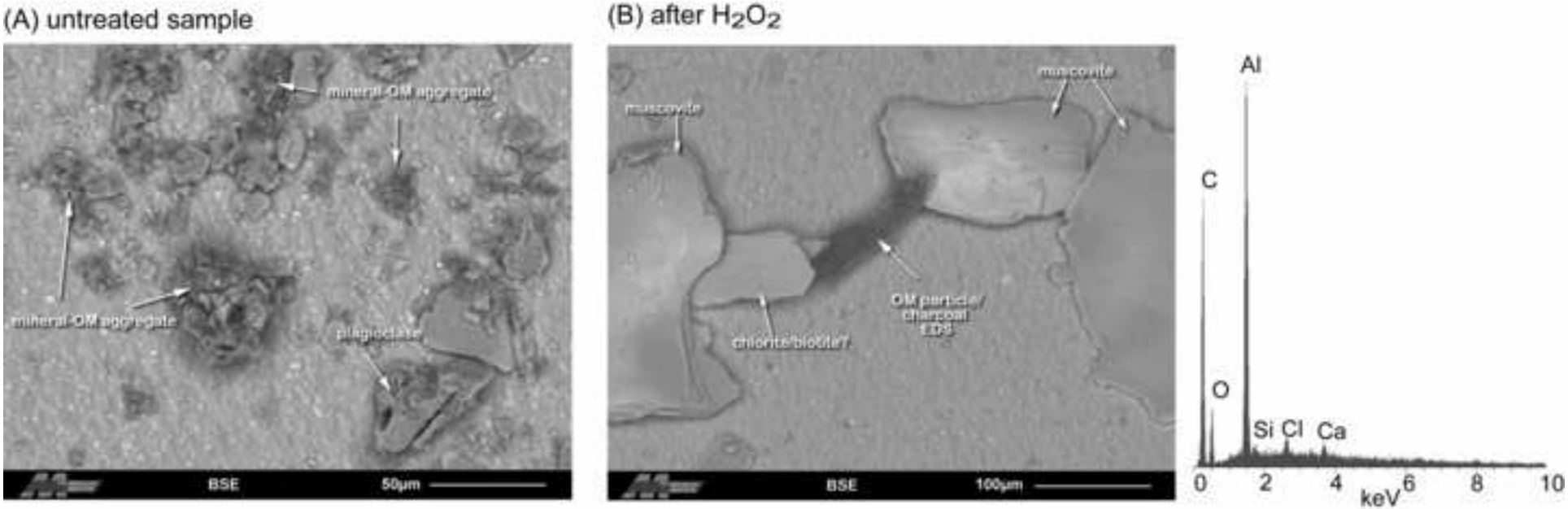

**Figure 5**

**Click here to download high resolution image**

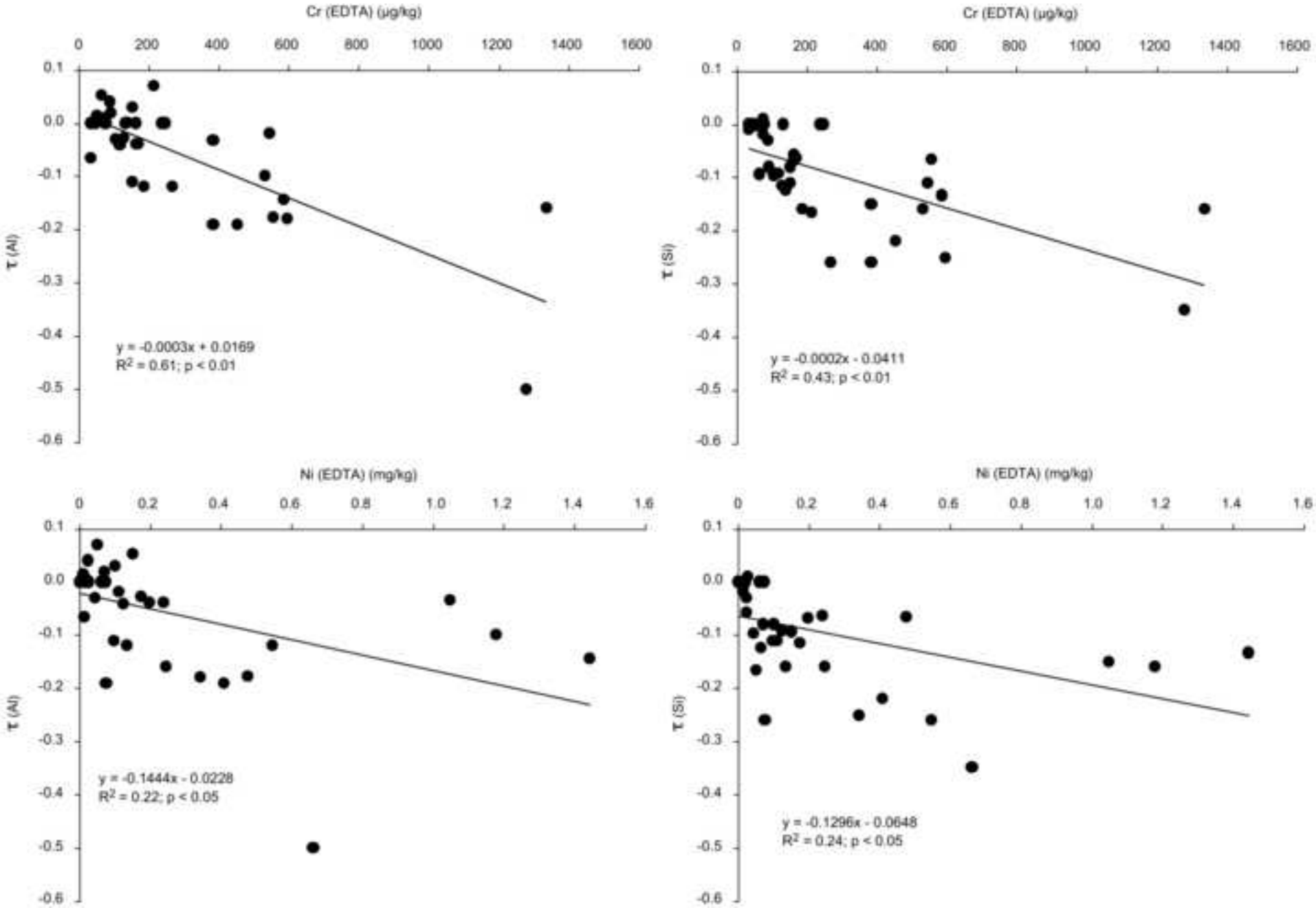

**Figure 6**

**Click here to download high resolution image**

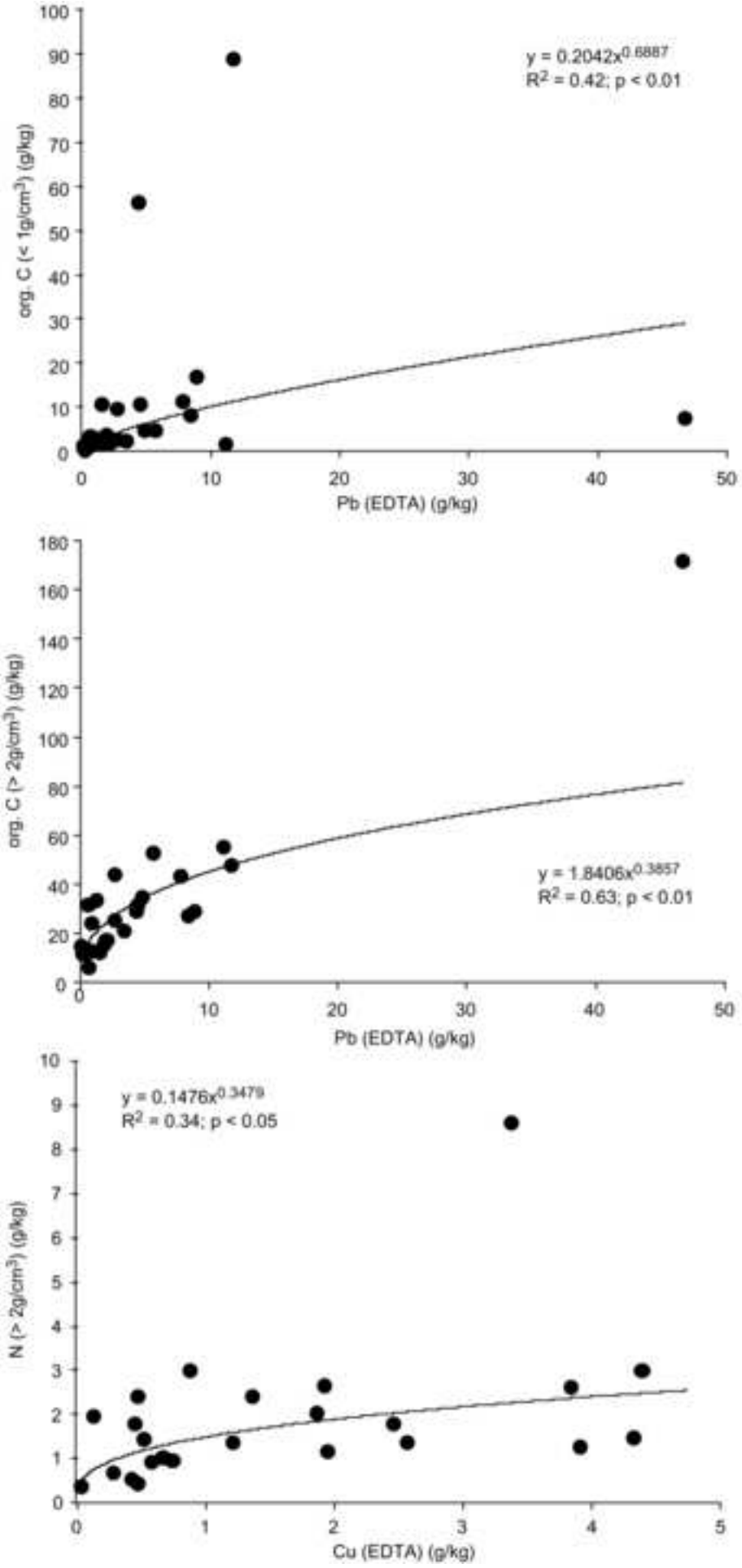

Figure 7

Click here to download high resolution image